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# Spectroscopic and magnetic studies of polynuclear Nd and heteronuclear Nd:Cu squarates

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## Abstract

Polynuclear Nd and heteronuclear Cu:Nd squarate complexes of the formulae $[Nd_2(C_4O_4)_3(H_2O)_{11}].2H_2O$ and $[Nd_2Cu(C_4O_4)_4(H_2O)_{16}].2H_2O$ were characterised in the 4.2 to 293 K temperature range by absorption spectroscopy. Electron transition probabilities were calculated and the splitting of $Nd^{3+}$ levels was determined. Magnetic susceptibility measurements were carried out in the range of 300 to 1.8 K. Optical and magnetic properties are discussed on the basis of X-ray data. The effect of d-electron ions in heteronuclear systems is evaluated by relation to the polynuclear neodymium squarate. The spectra of the solids are related to those of the respective solutions. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Neodymium; Copper; Squarates; Absorption spectroscopy; Luminescence; Magnetism

## 1. Introduction

During recent years increased interest has been devoted to studies of heteronuclear copper–lanthanide compounds. One of the reasons is that the presence of lanthanide ions effects the optical and magnetic properties of the system under investigation [1–7]. Moreover, interest in systems containing Cu and Ln ions is caused by the success in the synthesis of high temperature copper oxide superconductors [8,9].

Using appropriate ligands, heteronuclear complexes can be obtained, where the two metal centres, if paramagnetic, can interact with each other through the bridging groups in a ferromagnetic or antiferromagnetic way. One of the interesting ligands which is able to associate different cations of d and/or f-block elements is the squarate anion, $(C_4O_4)^{2-}$ [10–15]. Its planar tetradentate structure makes possible the creation of two-dimensional heterometallic and polynuclear systems.

Synthesis, crystal structure, magnetism and thermal behaviour of $[La_2Cu(C_4O_4)_4(H_2O)_{16}].2H_2O$ and $[Gd_2Cu(C_4O_4)_4(H_2O)_{12}].2H_2O$ were the subject of a paper by Bouayad et al. [1]. We investigated the EPR spectra of a $[Nd_2Cu(C_4O_4)_4(H_2O)_{16}].2H_2O$ single crystal [6].

Here we present the optical and magnetic results for Nd and Cu:Nd squarates. The latter is isostructural with the La:Cu complex, whereas neodymium squarate has the structure reported earlier in Ref. [12]. The reason for this choice was, among others, the rich and informative absorption spectrum of the $Nd^{3+}$ ion.

## 2. Experimental

Neodymium squarate, $[Nd_2(C_4O_4)_3(H_2O)_{11}].2H_2O$ (I) was prepared by the method reported in Refs. [10,12]. Single crystals of $[Nd_2Cu(C_4O_4)_4(H_2O)_{16}].2H_2O$ (II) were obtained from aqueous solution according to the procedure described in Ref. [1]. Although the same conditions as for the Gd:Cu complex synthesis were used, the crystals obtained are isomorphic with the La:Cu compound. They crystallize in the space group $P2_1/c$, $a=6.718(2)$, $b=32.301(3)$, $c=8.153(2)$ Å, $\alpha=89.88(2)$, $\beta=111.14(3)$, $\gamma=89.73(4)°$.

Absorption spectra were recorded at 293 and 4.2 K on a Cary-Varian 5 spectrophotometer equipped with a helium flow cryostat in the 400 to 1400 nm region. The intensities of the optical lines were calculated using the TAUS program and transformed to the oscillator strength values.

The magnetic susceptibility measurements were carried

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out with a SQUID magnetometer working down to 1.7 K, both in the low-field and high-field region.

## 3. Spectroscopic results

The absorption spectra of the single crystal of $[Nd_2Cu(C_4O_4)_4(H_2O)_{16}].2H_2O$ recorded at room temperature and 4 K are presented in Figs. 1 and 2, intensity analysis data are summarized in Table 1. In the same table the oscillator strength values of the electronic transition for the homonuclear compound (I) in paraffin oil are also shown (since we were not able to obtain crystals big enough for absorption measurements). Moreover, it includes also *P* values for aqueous solutions containing Nd, Cu and the squarate anion in ratios corresponding with that in crystals.

As it can be seen from Fig. 1, in the visible and IR region of the absorption spectrum of compound (II) the strongest broad band belongs to the d–d transition of $Cu^{2+}$, with the maximum at 780 nm (12,820 $cm^{-1}$) and it partially overlaps the neodymium f–f transitions (note that the concentration of Cu in the crystals is two times lower than that of neodymium). In the UV region, a strong charge transfer (CT) band overlaps the f–f transitions of $Nd^{3+}$ at energies higher than 490 nm (20,400 $cm^{-1}$). We were not able to record the CT band in the whole region, because it was too strong to be measured for the thickness of crystal used (0.237 mm). Therefore, the measurement of powdered crystals (II) in paraffin oil and of an aqueous solution containing Nd, Cu and squarate anions in ratios corresponding to those in (II) were also performed (see Fig. 3). The CT band for this solution has a maximum at about 382 nm (26,178 $cm^{-1}$) whereas the ligand band has a maximum at 325 nm. Oscillator strength for CT transition has a value equal to $300{,}200\times10^{-8}$ and is comparable to that recorded for the Cu–squarate solution ($293{,}200\times10^{-8}$).

Comparison of the UV region of the spectra for the Nd:Cu:sq solution with those for a single crystal of compound (II) shows a noticeable increase of absorption at the beginning (570 nm) of the CT band for (II); note that the preparation of the solution with the same concentration as in the crystal is impossible because of the low solubility of squarate complexes. A measurement for powdered crystals (II) in oil (see Fig. 3) allowed to find that the maximum of the CT band is localized at an energy of about 400 nm (25,000 $cm^{-1}$). Thus, it is possible to consider the creation of the CT state in a crystal at similar energies as in solutions. The minor shift of the CT state

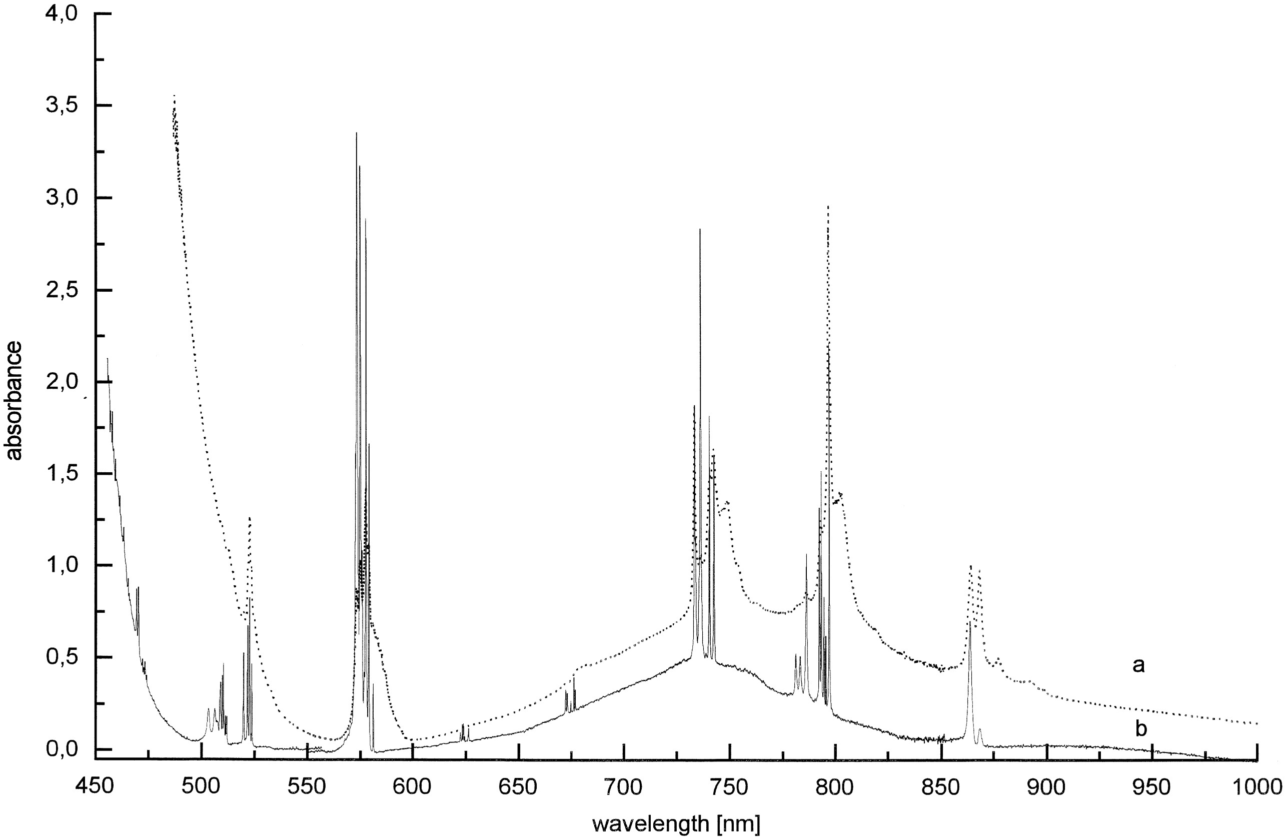

Fig. 1. Absorption spectra of the $[Nd_2Cu(C_4O_4)_4(H_2O)_{16}].2H_2O$ single crystal at 293 (a) and 4.2 K (b); ($l=0.237$ mm).

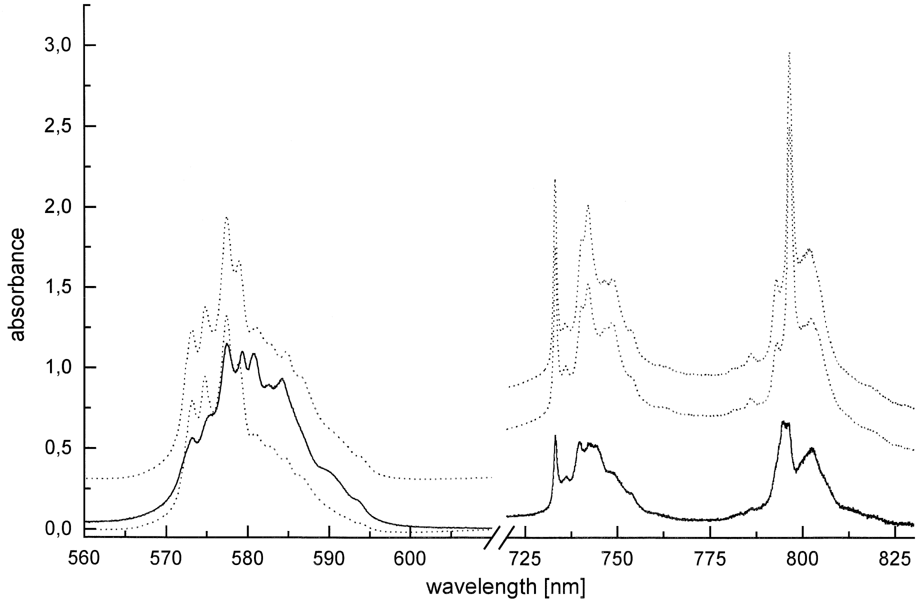

Fig. 2. Absorption spectra of the $[Nd_2Cu(C_4O_4)_4(H_2O)_{16}].2H_2O$ single crystal in different orientations (dotted lines) and of $[Nd_2(C_4O_4)_3(H_2O)_{11}].2H_2O$ powdered in paraffin oil (solid line); $T=293$ K.

can probably be caused by small differences in the structure of $Cu^{2+}$ surrounding or a stronger effect of the f-electron ion in solid.

When the temperature is going down to 4 K, the broad absorption band of $Cu^{2+}$ in the $[CuNd_2(C_4O_4)_4(H_2O)_{16}].2H_2O$ single crystal splits into two broad components with maxima at 737 nm (13,568 $cm^{-1}$) and 928 nm (10,775 $cm^{-1}$). The CT band shifts toward higher energies so it was possible to register $^2K_{13/2}$, $^4G_{7/2}$ and $^4G_{9/2}$ bands of $Nd^{3+}$ that was impossible at room temperature. Fine structure is observed for the f–f transitions of $Nd^{3+}$. The number of Stark components for the neodymium ion is consistent with the presence of only one structural position in the crystal structure as it was shown by Trombe et al. [1]. The analysis of the spectra at 4 K and of those at higher temperatures allows to propose the energy level diagram for $Nd^{3+}$ (see Table 2). It was found that the splitting of the $^4I_{9/2}$ ground state is equal to 362 $cm^{-1}$ similar to other systems where neodymium ions are nine-coordinated [16]. This splitting may be important for the explanation of the magnetic data at low temperatures.

Looking at the values collected in Table 1, one can see a big decrease in intensity of electronic transitions for crystal (II) on lowering the temperature, especially for the f–f transitions in regions where they are overlapped with $Cu^{2+}$ d–d transition ($^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^4S_{3/2}$). The decrease of intensity can be a result of the CF effect

Table 1
Oscillator strength values ($P\times10^8$) of electronic transitions for compound (I), (II), and aqueous solutions of Nd:Cu:sq

| $S'L'J'$ | Crystal (II) 293 K | Crystal (II) 4 K | Crystal (II) mean value | Comp. (I) in oil | Solution<br>$c_{Cu}=0.00125$<br>$c_{Nd}=0.0025$<br>$c_{sq}=0.005$<br>ref. squarate |
|---|---|---|---|---|---|
| $^4F_{3/2}$ | 327.0 | 109.5 | 360.5 | 320.1 | 253.8 |
| $^4F_{5/2}$, $^2H_{9/2}$ | 865.2 | 271.2 | 896.1 | 703.2 | 945.2 |
| $^4F_{7/2}$, $^4S_{3/2}$ | 952.1 | 366.4 | 953.2 | 767.1 | 946.1 |
| $^4F_{9/2}$ | 65.2 | 19.3 | 67.2 | 57.9 | 61.2 |
| $^2H_{11/2}$ | 22.1 | 18.3 | 20.3 | 19.8 | 16.9 |
| $^4G_{5/2}$, $^2G_{7/2}$ | 1660.2 | 1263.3 | 1947.2 | 1999.1 | 1325.5 |
| $^2K_{13/2}$,$^4G_{7/2}$, $^4G_{9/2}$ | | 431.5 | | 897.3 | |
| d–d of Cu 600–1350 (nm) | 23,697 | 13,173 | 24,815 | | 26,412 |
| CT 300–600 (nm) | Not measurable | | | | 300,200 |

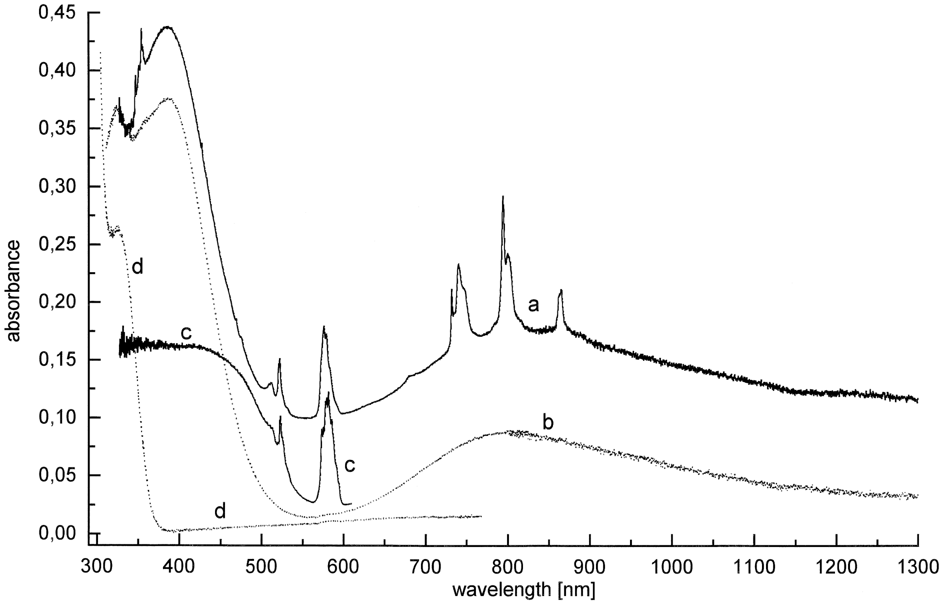

Fig. 3. Absorption spectra of: Nd:Cu:sq = 2:1:4 solutions ($c_{Cu}$ = 0.00125 M), reference sq solution (a), Cu:sq = 1:2 solution ($c_{Cu}$ = 0.00125 M), reference sq solution (b), compound (II) powdered in paraffin oil (c), squarate solution ($c$ = 0.00125 M), reference water (d).

Table 2
Experimental energy levels of $Nd^{3+}$ in the $[Nd_2Cu(C_4O_4)_4(H_2O)_{16}].2H_2O$ single crystal[a]

| Term | $E$ ($cm^{-1}$) | Term | $E$ ($cm^{-1}$) |
|---|---|---|---|
| $^4F_{3/2}$ | 11,579 | $^4G_{5/2}$ | 17,208 |
| | 11,516 | $^2G_{7/2}$ | 17,270 |
| | | | 17,313 |
| $^4F_{5/2}$ | 12,546 | | 17,369 |
| $^2H_{9/2}$ | 12,571 | | 17,393 |
| | 12,585 | | 17,441 |
| | 12,605 | | 17,461 |
| | 12,619 | | |
| | 12,717 | $^4G_{7/2}$ | 19,098 |
| | 12,768 | | 19,135 |
| | 12,801 | | 19,164 |
| | | | 19,238 |
| $^4F_{7/2}$ | 13,469 | | |
| $^4S_{3/2}$ | 13,508 | $^2K_{13/2}$ | 19,417 |
| | 13,585 | $^4G_{9/2}$ | 19,550 |
| | 13,627 | | 19,569 |
| | 13,635 | | 19,588 |
| | 13,641 | | 19,615 |
| | | | 19,646 |
| $^4F_{9/2}$ | 14,773 | | 19,657 |
| | 14,787 | | 19,692 |
| | 14,777 | | 19,712 |
| | 14,857 | | 19,755 |
| | 14,874 | | 19,872 |
| $^2H_{11/2}$ | 15,964 | $^2G_{9/2}$ | 21,097 |
| | 15,971 | | 21,132 |
| | 16,012 | | 21,155 |
| | 16,025 | | 21,177 |
| | 16,041 | | |
| | 16,064 | $^2D_{3/2}$ | 21,267 |
| | | | 21,303 |

[a] Splitting of the $^4I_{9/2}$: 0, 122, 177, 305, 358 $cm^{-1}$.

and/or vibronic coupling but it could also indicate the hetero ion effect in the spectra.

The differences in relative intensities of the separated Stark components are seen especially in the range of the $^4G_{5/2}$, $^2G_{7/2}$ band for two different orientations of the crystal (see Fig. 2). A comparison of the spectra of neodymium squarate in oil with single crystal spectra of (II) seems to confirm similarities in symmetry of $Nd^{3+}$ centre in both types of compounds (see Fig. 2). Also the intensities of the hypersensitive transition (Table 1) looks similar for both samples thus indicating a comparable structure of $Nd^{3+}$ site in both types of squarates. The analysis of the X-ray data (M–L distances and angles) leads to the same conclusion since on the basis of the fitting procedure by the Drew method [17], the coordination polyhedra may be described as distorted tricapped trigonal prisms [1,12].

Lower intensities of f–f bands for Nd:Cu:sq solution also compiled in Table 1 are reasonable since a concentration of the squarate complex is lower than the total concentration of the $Nd^{3+}$ ion [18].

## 4. Magnetic results

The free-ion ground state of Nd(III) is $^4I_{9/2}$. The first excited state, $^4I_{11/2}$, is located at an energy of about 2000 $cm^{-1}$, so at room temperature it is not populated. The Zeeman factor, $g$, is equal to 8/11. As a consequence of the free-ion approximation, the molar magnetic susceptibility for mononuclear species can be described by a relation given in Refs. [19,20] and $\chi_M \cdot T$ leads to the value of 1.64 $cm^3$ $mol^{-1}$ K. In the case of heteronuclear systems

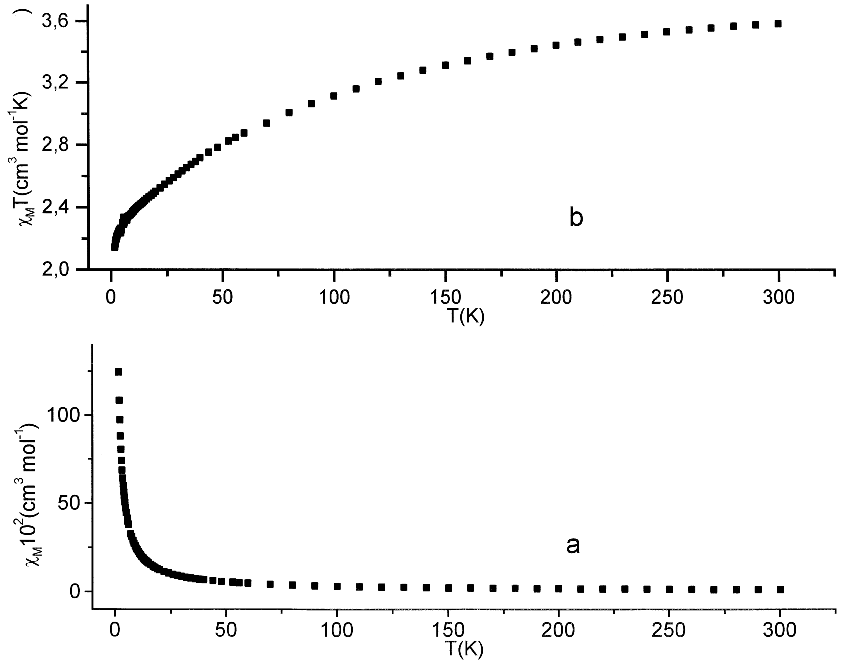

Fig. 4. Experimental magnetic data for compound (II) plotted as $\chi_M$ vs. $T$ (a) and $\chi_M \cdot T$ vs. $T$ (b).

one has to consider two different paramagnetic ions coupled in the complex. In fact, for $Nd^{3+}$ with the $f^3$ configuration angular and spin momenta are antiparallel in the $^4I_{9/2}$ free ion ground state ($J = L - S$) and a parallel alignment of the Nd(III) and Cu(II) spin momenta would lead to an antiparallel alignment of the angular momenta, i.e. to an overall antiferromagnetic interaction.

Figs. 4 and 5 show $\chi_M$ and $\chi_M \cdot T$ values versus $T$ for the $[CuNd_2(C_4O_4)_4(H_2O)_{16}].2H_2O$ and $[Nd_2(C_4O_4)_3(H_2O)_{11}].2H_2O$. At room temperature, $\chi_M \cdot T$ for (II) is equal to 3.582 $cm^3\ mol^{-1}$ K. Considering this system at room temperature as containing three independent metal ions, one can expect ~3.68 $cm^3\ mol^{-1}$ K for $\chi_M \cdot T$ (1.64 $cm^3\ mol^{-1}$ K for two isolated $Nd^{3+}$ ions and 0.4 for $Cu^{2+}$) according to reports of Kahn [21,22]. On lowering the temperature, $\chi_M \cdot T$ decreases continuously

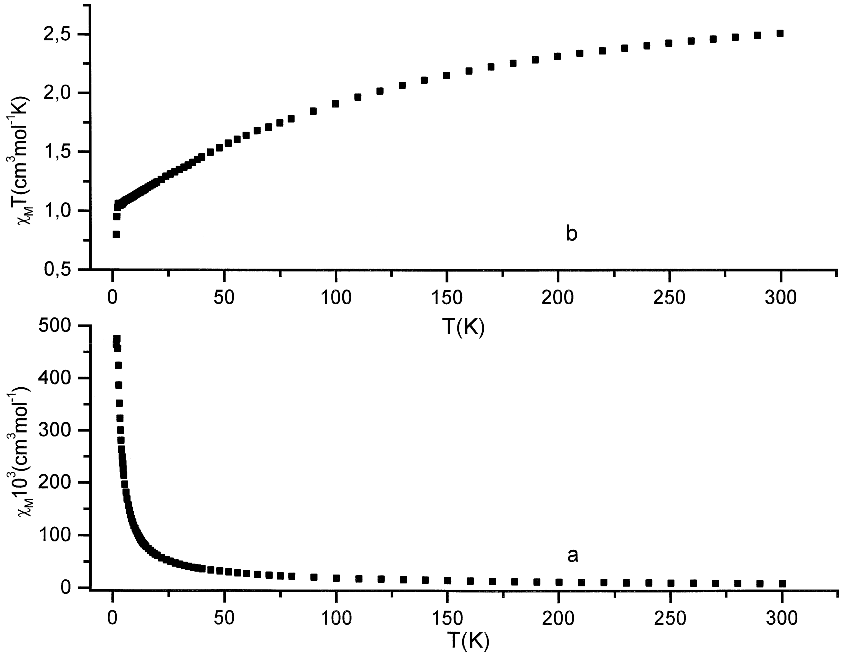

Fig. 5. Experimental magnetic data for compound (I) plotted as $\chi_M$ vs. $T$ (a) and $\chi_M \cdot T$ vs. $T$ (b).

Table 3
The magnetic data of compounds (I) and (II)[a]

| $T$ (K) | $\chi_M \times 10^3$ (I) ($cm^3\ mol^{-1}$) | $\chi_M \times 10^3$ (II) ($cm^3\ mol^{-1}$) | $\chi_M \cdot T$ (I) ($cm^3\ mol^{-1}\ K$) | $\chi_M \cdot T$ (II) ($cm^3\ mol^{-1} K$) | $\mu_{eff}$ (I) (BM) | $\mu_{eff}$ (II) (BM) |
|---|---|---|---|---|---|---|
| 1.72 | 464.7 | 1245 | 0.799 | 2.144 | 2.53 | 4.14 |
| 2.0 | 475.7 | 1085 | 0.952 | 2.169 | 2.76 | 4.17 |
| 4.0 | 263.8 | 565 | 1.056 | 2.259 | 2.91 | 4.25 |
| 20.0 | 62.2 | 125 | 1.246 | 2.500 | 3.16 | 4.48 |
| 40.0 | 36.4 | 67.9 | 1.457 | 2.717 | 3.42 | 4.67 |
| 60.0 | 27.3 | 47.9 | 1.641 | 2.876 | 3.62 | 4.80 |
| 90.1 | 20.5 | 34.0 | 1.847 | 3.064 | 3.85 | 4.95 |
| 100.2 | 19.1 | 31.1 | 1.908 | 3.115 | 3.91 | 4.99 |
| 150.3 | 14.3 | 22.0 | 2.152 | 3.314 | 4.15 | 5.15 |
| 200.2 | 11.5 | 17.2 | 2.314 | 3.443 | 4.30 | 5.25 |
| 250.3 | 9.7 | 14.1 | 2.425 | 3.530 | 4.40 | 5.32 |
| 280.3 | 8.8 | 12.7 | 2.478 | 3.569 | 4.45 | 5.35 |
| 300.3 | 8.3 | 11.9 | 2.511 | 3.582 | 4.49 | 5.36 |

[a] $\theta$ (I) $= -47.46$, $\theta$ (II) $= -20.10$; temperature range 40–300 K.

and tends to 2.144 $cm^3\ mol^{-1}$ K as $T$ approaches 1.7 K (see Table 3). The magnetic behaviour follows the Curie–Weiss law in the range 40 to 300 K with $\theta = -20.11$ K. The negative value of the $\theta$ can indicate antiferromagnetic ordering but the squarate ligand does not give a chance for a strong short range M–M coupling even in the dinuclear Cu–squarato complexes [23]. The deviation of the magnetic susceptibility with respect to the Curie law can be due to the crystal field which splits the $^4I_{9/2}$ term into five Kramer's doublets. The temperature decrease leads to progressive depopulation of the higher energy components of the ground state multiplet.

As was demonstrated in the crystal structure data, the crystals (II) are isomorphic with LaCusq ones [1], thus, interaction inside $(CuNdNdCu)_\infty$ fragment besides the Cu–Cu interaction realised by the hydrogen bonding must be considered, too. The system can be treated as two-dimensional and the interaction of every $Nd^{3+}$ ion with two others and also with Cu ions should be taken into account. An analysis of the interaction between Nd–Cu ions only in the chain leads to two different chains with opposite ordering of copper spins. Considering this model, the coupling constant $J$ determined on the basis of EPR investigations is equal to 0.2 and 0.1–0.2 $cm^{-1}$ for Nd–Cu and Cu–Cu, respectively [6]. If Nd:Cu, Nd:Nd and Cu:Cu interactions are considered, a very complex relation for $\chi_M \cdot T$ in the heteronuclear system can be obtained. In fact, the results for both magnetic susceptibility and magnetic moment cannot be analysed neglecting Nd–Nd interaction as it was suggested from the magnetic behaviour of simple neodymium squarate. As can be seen from data collected in Table 3, the magnetic moment for (I) is lower than that for the isolated neodymium system. The $\theta$ is negative and is equal to $-16.70$ K which confirms the antiferromagnetic ordering in (I).

Note also that the lanthanide ion in both polynuclear neodymium and heteronuclear (Cu:Nd) systems occupies sites with low symmetry close to $C_{2v}$ (CN$=$9, a distorted TCTP polyhedron) [1,12]. Thus at temperatures low enough the lowest Kramer's doublet is thermally populated and it is possible to attribute the effective spins as equal to 1/2. Assuming that both Nd–Nd and Cu–Cu interactions are weak and antiferromagnetic, the value of $\chi_M \cdot T$ versus $T$ must be considerably lower at 1.7 K than at room temperature as it is seen in Figs. 4 and 5. It is worth noting that the results obtained for the investigated polynuclear squarates confirm our above consideration.

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