A Cationic Tetranuclear $[Ni^{II}_4(MeOH)_2(pko)_6]^{2+}$ Cluster Showing Antiferro- and Ferromagnetic Features

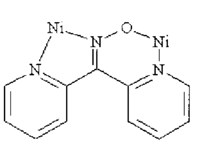
Maria Alexiou,[a] Catherine Dendrinou-Samara,[a] Catherine P. Raptopoulou,[b] Aris Terzis,[b] Vassilis Tangoulis,*[c] and Dimitris P. Kessissoglou*[a]

Keywords: Cluster compounds / Magnetic properties / Oximato ligands / Nickel

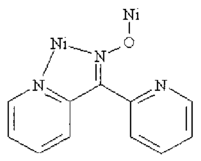
The majority of reported nickel tetranuclear clusters have a dicubane-like structural core. The compound presented here is the second example possessing an Ni_4O_2 core based on a chair or butterfly "out-of-face" topology. This compound also belongs to the family of compounds characterized as metallacrowns with an $[Ni–N–O–]_n$ linkage and is the only example with three Ni–O–N–Ni strands bridging the nickel atoms. The values obtained from the fitting procedure are $J_1 = 55.8$ cm^{-1}, $J_2 = –67.2$ cm^{-1}, $g = 2.2$, $\rho = 1.1\%$. These values suggest the presence of both ferromagnetic and antiferromagnetic interactions, while a small paramagnetic impurity is also present. This magnetic behaviour with antiferromagnetic internal coupling and ferromagnetic spin-alignment is the second example in the literature and the first in the metallacrown family.

Introduction

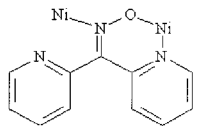
Our interest in polynuclear nickel[1−4] or manganese[5−10] complexes showing interesting structural and magnetic features has focused especially on metallacrowns, a molecular class that exhibits selective recognition of cations and anions. An attractive feature of metallacrowns is that they concentrate a large number of metal ions into a small area. These large concentrations of metal ions may lead to interesting magnetic behaviour.[1,10−12] The structural features of each metallacrown can lead to high magnetic moments per compound through ferromagnetic exchange or coupling to low-lying paramagnetic states. Previously reported metallacrowns[1−27] have been prepared using hydroxamic acids and/or ketone oximic acids as constructing ligands. Hpko is a bifunctional ligand that can bind metal atoms in either five- or six-membered chelate rings. The deprotonated di-2-pyridyl ketone oxime can act in two binding modes: (i) bichelate and (ii) monochelate. In (i) the ketone oxime oxygen atom (O_k) and one pyridine nitrogen atom (N) bind to one metal atom and the other pyridine nitrogen atom (N) plus the ketone oxime nitrogen atom (N_k) chelate an adjacent metal atom in a *syn-anti* arrangement (form A). In (ii) the ketone oxime nitrogen atom (N_k) and one pyridine nitrogen atom (N) are coordinated to one metal atom in a five-membered chelate ring in a *syn-syn* arrangement (form B_1) or the ketone oxime oxygen atom (O_k) and one pyridine nitrogen atom (N) are bound to one metal atom in a six-membered chelate ring in a *syn-anti* arrangement (form B_2). These juxtaposed five- and six-membered chelate rings form the basis of the metallacrown ring through the $[M-N-O-]_n$ linkage.



form A



form B_1 (*syn-syn*)



form B_2 (*syn-anti*)

For tetranuclear nickel clusters the majority of the compounds reported have a dicubane-like structural core[28−41] with only one example possessing an Ni_4O_2 core based on a chair or butterfly "out-of-face" topology.[42] The compound presented here is the second example that may be characterized as having a chair topology and the only example showing a metallacrown $[M-N-O-]_n$ linkage with three Ni−O−N−Ni strands bridging the nickel atoms. This compound is also the first metallacrown showing antiferromagnetic internal coupling and ferromagnetic spin alignment.

Results and Discussion

The reaction of $Ni(ClO_4)_2$ with dipyridyl ketone oxime, $(2\text{-py})_2C=NOH$ (Hpko) in a 1:1 ratio in methanol in the

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[a] Department of General and Inorganic Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki,
54124 Thessaloniki, Greece
[b] NCSR "Demokritos", Institute of Materials Science,
15310 Aghia Paraskevi Attikis, Greece
[c] Department of Materials Science, University of Patras,
26500 Patras, Greece

presence of NaOH gives red-brown crystals of the cluster $[Ni^{II}_4(CH_3OH)_2(pko)_6](OH)(ClO_4)\cdot 2CH_3OH\cdot 4H_2O$ (**1**) after slow evaporation of the solvent. The synthesis of cluster **1** was achieved by the reaction

$$4\ Ni(ClO_4)_2 + 6\ Hpko + 7\ NaOH \xrightarrow{Methanol} [Ni(II)_4(CH_3OH)_2(pko)_6](OH)(ClO_4) + 7\ NaClO_4 + 6\ H_2O$$

The compound crystallizes in the tetragonal space group *P*4/*n*. The asymmetric unit contains half of the tetranuclear cation, half a perchlorate and hydroxide counterion, two lattice water molecules and one methanol solvent molecule of crystallization. The tetranuclear $[Ni^{II}_4(pko)_6(CH_3OH)_2]^{2+}$ cation is centrosymmetric; the inversion center lies in the center of the Ni(2)−O(1)−Ni(2)−O(1) moiety. The whole structure can be characterized as having a "metallacrown chair" topology (Figure 1). Two nickel atoms with a distorted octahedral NO_5 coordination environment are bridged by two oxygen atoms from pko ligands to form the Ni_2O_2 core, in which the Ni(2)−O(1) or Ni(2)−O(1)# distances are found to be 2.086(8) Å and 2.101(8) Å, respectively, the Ni(2)···Ni(2)# and O(1)···O(1)# separations to be 3.059 Å and 2.861 Å, respectively, and the Ni(2)−O(1)−Ni(2)# and O(1)−Ni(2)−O(1)# angles to be 93.70° and 86.16°, respectively (Table 1). Each nickel atom of the Ni_2O_2 core is bound to two oximato oxygen atoms with Ni(2)−O(11) and Ni(2)−O(21) distances of 1.974(9) and 2.047(8) Å, respectively; the octahedron is completed by a methanol oxygen atom at a distance of 2.113(8) Å.

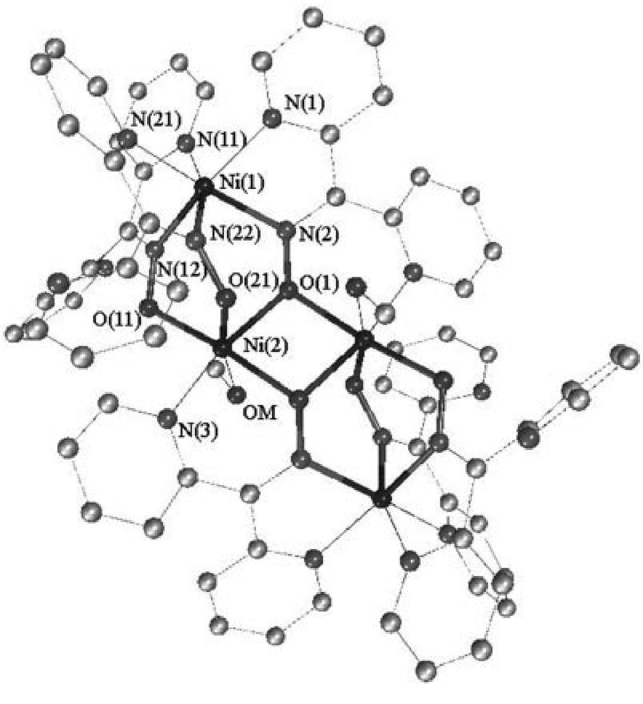

Figure 1. Crystal structure of the the $[Ni^{II}_4(pko)_6(CH_3OH)_2]^{2+}$ ion; the core and ring connectivity have been highlighted; perchlorate and hydroxy ions are not shown

Table 1. Selected bond lengths [Å] and angles [°] of **1**

Bond lengths			
Ni(1)−N(12)	2.025(10)	Ni(2)−O(11)	1.974(9)
Ni(1)−N(22)	2.040(11)	Ni(2)−N(3)#1	2.036(10)
Ni(1)−N(2)	2.043(10)	Ni(2)−O(21)	2.047(8)
Ni(1)−N(11)	2.100(10)	Ni(2)−O(1)	2.086(8)
Ni(1)−N(1)	2.107(11)	Ni(2)−O(1)#1	2.101(8)
Ni(1)−N(21)	2.108(11)	Ni(2)−OM1	2.113(8)
Ni(2)···Ni(2)#1	3.059	O(1)···O(1)#1	2.861
Ni(1)···Ni(2)	3.469		
Angles			
N(22)−Ni(1)−N(11)	163.3(4)	O(11)−Ni(2)−O(1)#1	174.7(3)
N(12)−Ni(1)−N(1)	164.7(4)	O(21)−Ni(2)−OM1	169.2(4)
N(2)−Ni(1)−N(21)	163.2(4)	N(3)#1−Ni(2)−O(1)	169.9(4)
N(2)−O(1)−Ni(2)#1	93.70(4)	O(1)−Ni(2)−O(1)#1	86.16(4)

Symmetry operation: #1: −*x*, 1−*y*, 1−*z*

Two pko oximato moieties bridge the core nickel atom with the "wing" nickel atom in a monochelate mode and a *syn-syn* arrangement(form B_1), while the third pko ligand bridges the "wing" nickel atom Ni(1) and the symmetrically equivalent Ni(2)# nickel atom through the oximato moity in bichelate mode and a *syn-anti* arrangement (form A). The two "wing" nickel atoms have a pure N_6 coordination environment with three nitrogen atoms coming from three oximato moieties $[Ni(1)-N_{oximato}$ (av.) = 2.036 Å] and three nitrogen atoms from three pko-pyridine groups $[Ni(1)-N_{pyridine}$ (av.) = 2.105 Å]. Four of the six pko ligands have the second pyridine nitrogen atom uncoordinated. The "wing" nickel atoms Ni(1) and Ni(1)# lie on opposite sides of the Ni_2O_2 parallelogram at 3.469 Å and 4.744 Å from the core nickel atoms Ni(2). The formation of the 12-membered metallacrown follows the pattern (Ni−N−O−Ni−O−N−Ni−N−O−Ni−O−N) and, in cooperation with the *syn-anti* mode of one pko-oximato ligand, allows the construction of the chair-like metallacrown shape.

Magnetic Study

The temperature dependence of the susceptibility data in the form of χ_M and $\chi_M T$ vs. T plots is shown in Figure 2.

The room-temperature value of $\chi_M T$ is 3.5 emu·mol^{-1}·K lower than the value expected for four uncorrelated $S = 1$ spins (4.0 emu·mol^{-1}·K for $g = 2.0$) showing that an overall antiferromagnetic behavior characterizes the magnetic interaction between the magnetic centers. As the temperature decreases the value of $\chi_M T$ also decreases until about 17 K, where its value is close to zero. After that temperature a plateau forms until 2 K, revealing that a paramagnetic impurity is present. This is shown better in the χ_M data, where a Curie tail appears below 7 K. Another important aspect of the χ_M data is the peak at about 67 K, which is evidence of different types of interaction in the cluster.

Magnetization measurements were carried out in the field range 0−12 T at 2 K in order to verify the ground state and possibly to observe a jump to an excited state (Figure 3). The reduced magnetization at 12 T is 0.0135 μ_B and this is

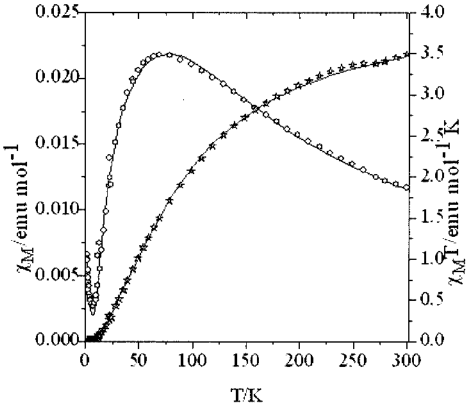

Figure 2. Temperature dependence of the susceptibility data in the form of χ_M (open circles) and $\chi_M T$ (open stars) vs. T plots in an applied field of 0.1 T; the solid lines represent the best fit according to Equation (1) (see text for details)

due to the paramagnetic impurity of the system; there is no population of the excited state with $S_{tot} > 0$ until 12 T.

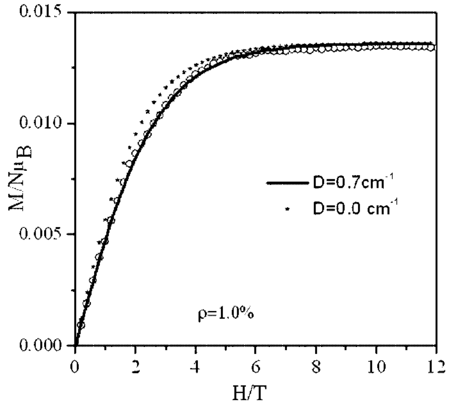

Figure 3. Magnetization data at 2 K and in the field range 0−12 T; the lines represent 1.0% of an $S = 1$ system with $D = 0$ cm^{-1} (dotted) and $D = 0.7$ cm^{-1} (solid)

The safe conclusions from the study of the magnetic experiments are: (a) there are both ferro- and antiferromagnetic interactions in the cluster, which lead to an overall antiferromagnetic behavior; (b) the ground state of the system is $S = 0$ with a small percentage of paramagnetic impurity of an $S = 1$ system.

In order to calculate the interactions between the magnetic ions the zero-field Hamiltonian according to Equation (1) was used, where the numbering of the spins and the exchange couplings are based on the magnetic model in Figure 4, according to crystallographic criteria.

$$H = J_1(S_1S_2 + S_3S_4) + J_2(S_2S_3) + J_3(S_1S_3 + S_2S_4) \qquad (1)$$

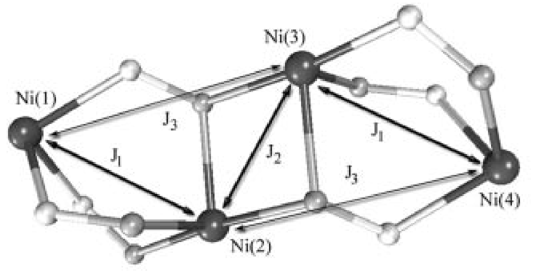

Figure 4. The magnetic model showing the interaction vectors; Ni(3) and Ni(4) are symmetry equivalents of Ni(2) and Ni(1), respectively

The fitting results are shown in Figure 2 in the form of solid lines and the values obtained are: $J_1 = 48.1$ cm^{-1}, $J_2 = -12.1$ cm^{-1}, $J_3 = 14.5$ cm^{-1}, $g = 2.2$, $\rho = 1.1\%$.

The interaction between the two central ions Ni(2) and Ni(3) is ferromagnetic, which is in accordance with the Ni−O−Ni angle (93.7°) and the small distance between the two ions (3.059 Å), while the interaction between Ni(1) and Ni(2) and Ni(3) and Ni(4) is antiferromagnetic due to the superexchange pathway [Ni(1)−N−O−Ni(2)] and the long distance between the magnetic ions (3.470 Å).

It is interesting to note that a third antiferromagnetic interaction exists between Ni(1) and Ni(3) and Ni(2) and Ni(4) despite the long distance between the Ni ions (4.743 Å). A ferromagnetic Ni−Ni interaction is observed when the Ni−O−Ni angle is close to orthogonal. Antiferromagnetic interactions have also been observed for Ni−O−Ni bridging angles larger than 99°. Following the lead of Christou et al.,[43] for comparison purposes the magnetic interactions (J) are represented in Figure 5 as a function of average Ni−O−Ni angles.

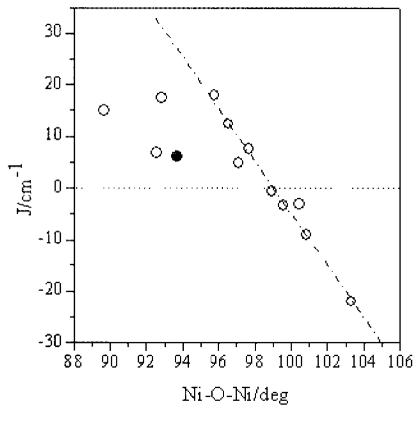

Figure 5. Exchange interaction (J) as a function of the Ni−O−Ni angle for different cores of the type Ni_4O_4 described in the literature (open circles)[36] and that reported in this contribution (solid circle)[44]

The energy scheme according to the previous parameters reveal that the ground state is $S = 0$, and that this is well separated from the first excited state ($S = 1$, $\Delta E = 36$ cm^{-1}; Figure 6).

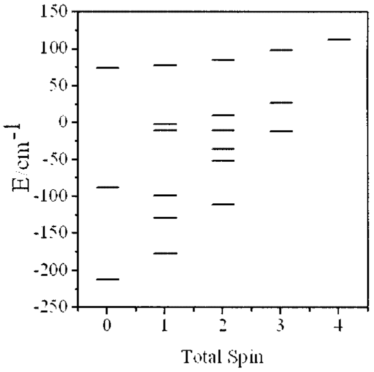

Figure 6. Energy scheme of the magnetic model according to fitting results (see text for details)

Concerning the magnetization data, a simulation procedure was carried out in order to obtain information about the paramagnetic impurity. Assuming that the ground state $S = 0$ is well isolated (which is true according to the susceptibility data) at 2 K the magnetization curve belongs to the paramagnetic impurity of an $S = 1$ system. The simple Brillouin function of a 0.008% $S = 1$ state is not completely superimposed on the data, which implies that the zero-field term may play an important role. By adding the zero-field term the best simulation was obtained for a D value of 0.7 cm^{-1}.

Conclusions

While tetranuclear nickel clusters have been reported, the compound presented here shows some very interesting features. It is the second example possessing an Ni_4O_2 core based on a "chair or butterfly out-of-face" topology. This compound also belongs to the family of compounds characterized as metallacrowns with an $[Ni-N-O-]_n$ linkage and is the only example with three strands Ni−O−N−Ni bridging the nickel atoms. The magnetic study shows the presence of both ferromagnetic and antiferromagnetic interactions. The magnetic behaviour with antiferromagnetic internal coupling and ferromagnetic spin alignment is the second example in the literature and the first in the metallacrown family.

Experimental Section

CAUTION: *Perchlorate compounds of metal ions are potentially explosive; only a small amount of material should be prepared and handled with caution!*

Materials: The chemicals for the synthesis of the compounds were used as purchased. DMF was distilled from calcium hydride (CaH_2) and CH_3OH from magnesium (Mg); they were both stored over molecular sieves (3 Å). Hpko and $Ni(ClO_4)_2 \cdot 6H_2O$ were purchased from Aldrich Co. All chemicals and solvents were reagent grade.

Physical Measurements: Infrared spectra (200−4000 cm^{-1}) were recorded with a Perkin−Elmer FT-IR 1650 spectrometer with samples prepared as KBr pellets. UV/Vis spectra were recorded with a Shimadzu-160A dual-beam spectrophotometer. C, H and N elemental analysis was performed with a Perkin−Elmer 240B elemental analyser; Ni was determined by atomic absorption spectroscopy with a Perkin−Elmer 1100B spectrophotometer. Electrical-conductance measurements were carried out with a WTW model LF 530 conductivity outfit and a type-C cell, which had a cell constant of 0.996. This represents a mean value calibrated at 25 °C with potassium chloride. The temperature dependence of the magnetic susceptibility was measured on polycrystalline powder samples using a Cryogenics S600 SQUID Magnetometer with an applied field of 0.1−1.0 T in the temperature range 2−300 K. Data were corrected for sample-holder contribution and diamagnetism of the sample using standard procedures.

Synthesis of $[Ni^{II}_4(CH_3OH)_2(pko)_6](OH)(ClO_4) \cdot 2CH_3OH \cdot 4H_2O$ (1): Dipyridyl ketone oxime (1.19 g, 6 mmol) was added to a solution of sodium hydroxide (0.24 g, 6 mmol) in CH_3OH (20 mL). The resulting mixture was stirred for 1 h, generating a pale-yellow solution. $NiClO_4 \cdot 6H_2O$ (1.46 g, 4 mmol) dissolved in CH_3OH (20 mL) was then added with stirring. The resulting red-brown solution was stirred for 1 h. Brown crystals suitable for X-ray diffraction studies were obtained by slow concentration. Yield 50%. $C_{70}H_{73}ClN_{18}Ni_4O_{19}$ (1740.8): calcd. C 48.3, H 4.2, N 14.5, Ni 13.4; found C 47.9, H 4.4, N 14.2, Ni 13.0. IR: $\tilde{\nu}$ = 1597 [vs, ν(C=N)], = 1462 [vs, ν(N=O)] cm^{-1}. UV/Vis (DMF): λ_{max} (ε [dm^3·mol^{-1}·cm^{-1}]) = 524 (722, sh) nm.

X-ray Crystal-Structure Determination: Slow crystallization of **1** from methanol yielded red prismatic crystals. A crystal with approximate dimensions 0.08 × 0.25 × 0.40 mm was mounted in a capillary. Diffraction measurements were made with a $P2_1$ Nicolet diffractometer upgraded by Crystal Logic using graphite-monochromated Cu radiation. Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $22° < 2\theta < 54°$. These data are given in Table 2. Intensity data were recorded using a θ-2θ scan to $2\theta(\max) = 100°$ with a scan speed of 1.5°/min and scan range 2.4 plus $\alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and ψ-scan absorption corrections were applied using the Crystal Logic software. Symmetry-equivalent data were averaged with $R = 0.0703$ to give 4442 independent reflections from a total of 4725 collected. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares techniques on F^2 with SHELXL-93 using 4442 reflections and refining 518 parameters.[45−47] The final values for $R1$, $wR2$ and GOF for observed data are given in Table 2, and for all data are 0.1724, 0.3409 and 1.057 respectively. The maximum and minimum residual peaks in the final difference map were 1.123 and −0.599 e/Å. The largest shift/esd in the final cycle was 0.017. CCDC-223110 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]. Structural remarks: The crystals were small and of poor quality (the peak scans showed small shoulders). For this reason we did not collect data above $2\theta = 100°$, and even for the data we did collect about 40% was unobserved. This problem is due especially to disordered perchlorate and hydroxy anions and solvent molecules. The quality of the $[Ni^{II}_4(pko)_6(CH_3OH)_2]^{2+}$ ion is very satisfactory, particularly for interpreting the magnetic data. All hydrogen atoms of the pko ligands were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically. The perchlorate counterion was refined as follows: two independent chlorine atoms were found in the difference Fourier map, one located on a fourfold axis of symmetry, Cl(1), and the second on a fourfold inverse axis of symmetry, Cl(2). One of the oxygen atoms on Cl(1), O(31), is also located on the fourfold axis of symmetry, while the other three oxygen atoms, O(32), O(33), O(34), are on general positions and were refined with occupation factor 0.25 as disordered over the C_4 axis. Only one oxygen atom, O(41), was found near Cl(2), generating the perchlorate anion due to the fourfold inverse axis of symmetry. Atoms Cl1 and Cl2 were refined anisotropically, while all oxygen atoms were refined isotropically. The hydroxide counterion was refined as follows: two independent oxygen atoms were found in the difference Fourier map, both located on a fourfold axis of symmetry and were refined isotropically with occupation factors 0.25. The water and methanol solvent molecules were refined isotropically as follows: one of the water molecules, OW(1), was found disordered and it was refined over three positions with occupation factors of a total sum one. The second water molecule, OW(2), was also found disordered and it was refined over two positions with occupation factors of a total sum one. The methyl group of the methanol solvate was found disordered and it was refined over three positions with occupation factors of a total sum of one.

Table 2. Summary of crystal, intensity collection and refinement data of **1**

Empirical formula	$C_{70}H_{73}ClN_{18}Ni_4O_{19}$
Formula mass	1740.75
Temperature [K]	293
Radiation (Cu-K_α) [Å]	1.54180
Crystal system, space group	tetragonal, $P4/n$
a [Å]	22.798(2)
b [Å]	22.798(2)
c [Å]	16.633(2)
Volume [Å^3]	8645(2)
Z, calculated density [Mg/m^3]	4, 1.337
Absorption coefficient [mm^{-1}]	1.874
Crystal size [mm]	0.40 × 0.25 × 0.08
Reflections collected/unique	4725/4442 [$R_{int} = 0.0703$]
Data/restraints/parameters	4442/22/518
R_{int} [2528 refls. with $I > 2\sigma(I)$]	$R1 = 0.1035$, $wR2 = 0.2600$
R_{int} (all data)	$R1 = 0.1724$, $wR2 = 0.3409$

Acknowledgments

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[44] In order to compare our results (J-formalism, $H = J_{ij}\ S_iS_j$) with the other ones shown in Figure 5 ($-2J$-formalism, $H = -2J_{ij}\ S_iS_j$) we had to convert our value of $J_2 = -12.1\ \mathrm{cm^{-1}}$ to $J_2' = 6.05\ \mathrm{cm^{-1}}$.

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