Crystal Structure, Second Harmonic Generation, and Vibrational Spectroscopy of $K_2Mg_2(SCN)_6{\cdot}3H_2O$[†]

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Single crystals of $K_2Mg_2(SCN)_6{\cdot}3H_2O$ were obtained by the reaction of the binary compounds $MgCl_2{\cdot}xH_2O$ and KSCN at 220° using the Bridgman technique. The compound crystallizes hexagonally with the noncentrosymmetric space group $P6_3cm$ ($Z = 2$, $a = 885.2(1)$ pm, $c = 1732.7(3)$ pm, $R1_{all} = 0.1035$). In the crystal structure, the Mg^{2+} ions are coordinated by oxygen and nitrogen atoms while the K^+ ions are exclusively surrounded by sulfur atoms. The two crystallographically different Mg^{2+} ions are linked via common nitrogen atoms to dimers, $[Mg_2(SCN)_6(H_2O)_3]^{2-}$. The K^+ ions are connected with each other by two crystallographically different sulfur atoms to hexagonal rings which form layers in the (001) plane. The dimers are connected to these layers in equal orientation leading to the absence of inversion symmetry. Frequency doubling measurements on $K_2Mg_2(SCN)_6{\cdot}3H_2O$ as well as on KDP powder samples were carried out. The second harmonic generation intensity of the rhodanide is about 40% of that of KDP. Furthermore, IR and Raman measurements were performed, and the results were compared to other thiocyanates. The energies of the vibrations of the molecular SCN^- ions demonstrate their bridging function in the crystal structure, and the energies and the shapes of the H_2O bands indicate hydrogen bonds.

Introduction

Because of their very intense parity allowed $4f^65d^1 \rightarrow 4f^7$ luminescence, Eu^{2+} ions are of interest for several applications such as blue phosphors in discharge lamps or X-ray storage phosphors.[1] In addition, the energy, e.g., the color of the emission, depends very strongly on the surroundings. Above all, the kind of ligand is of importance. While Eu^{2+} doped in oxidic or chloridic host lattices shows emission almost in the UV or blue region,[2] more covalent ligands such as sulfur or nitrogen should shift the emission to longer wavelengths due to the nephelauxetic effect. In contrast to the recent interest in efficient phosphors which emit red or green radiation for the development of bright LEDs, studies dealing with the optical properties of Eu^{2+} ions doped in nitrides are very limited.[3,4] Thus, we started recently to investigate the luminescence of Eu^{2+} in thiocyanate host lattices. Additionally, it is of interest to compare the influence of the more ionic ligand SCN^- to those of more covalent nitrides or sulfides. For this purpose, we characterized the isotypic pseudobinary earth alkaline thiocyanates $M(SCN)_2$ (M = Ca, Sr, Ba, Eu).[5,6] The cations are 8-fold coordinated in the form of squared antiprisms by four sulfur and four nitrogen atoms. Luminescence measurements of $M(SCN)_2{:}Eu^{2+}$ (M = Sr, Ba) show indeed a very bright deep green emission at low temperatures.[7,8] To investigate the influence of only one ligand, sulfur or nitrogen, we prepared now a new compound with a hard and a soft cation which should coordinate exclusively to nitrogen and sulfur, respectively, according to Pearson's concept. Indeed, in $K_2Mg_2(SCN)_6{\cdot}3H_2O$ the K^+ ions are surrounded only by sulfur atoms, and the Mg^{2+} ions are connected to the thiocyanate ligands exclusively by the nitrogen atoms. Therefore, the luminescence properties of the title compound doped with Eu^{2+} ions should be of interest for the comparison to the luminescence of Eu^{2+} doped "binary" earth alkaline rhodanides. A respective work will be reported soon.

The crystal structures of the anhydrous thiocyanates of the alkaline metals MSCN are determined for M = Na, K, Cs.[9−11] In contrast, the rhodanides of the alkaline earth elements crystallize from aqueous solution in the form of their dihydrates, $Ba(SCN)_2{\cdot}2H_2O$,[12] trihydrates, $M(SCN)_2{\cdot}3H_2O$ (M = Sr, Ba),[13,14] or tetrahydrates, $M(SCN)_2{\cdot}4H_2O$ (M = Mg, Ca).[15,16] Furthermore, we were

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[†] Dedicated to Professor Kurt Klepp on the occasion of his 60th birthday.

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successful in the preparation of the dihydrate of calcium rhodanide.[6] The anhydrous alkaline earth rhodanides $M(SCN)_2$ (M = Ca, Sr, Ba) could be obtained by metathesis from NaSCN and MCl_2 for M = Sr, Ba, or by dehydration of the hydrated species.[5,6] In contrast, the reaction of NaSCN and $MgCl_2$ yielded not the “binary” magnesium thiocyanate but $Na_4Mg(SCN)_6$.[17] While the Mg^{2+} ions are exclusively coordinated by nitrogen atoms, in this case the Na^+ ions are surrounded by both sulfur and nitrogen atoms. To prepare a compound with only one kind of atom in the coordination sphere because of the reasons described above, we tried to synthesize a ternary magnesium rhodanide with potassium, which should, according to Pearson’s concept, fulfill these requirements. Because of the insufficient drying of the educts, we obtained a water containing compound instead. In the present publication, we present the synthesis and the crystal structure of $K_2Mg_2(SCN)_6{\cdot}3H_2O$. Additionally, we recorded IR as well as Raman spectra and compared the vibrational energies to these of other thiocyanates. Because of the noncentrosymmetric space group $P6_3cm$ and the large polarizability of the soft ligands, a high SHG (second harmonic generation) effect could be expected. This forced us to perform frequency doubling measurements on powder samples. For an estimation of the intensity of the effect, identical measurements on powder samples of the frequently used frequency doubling material KDP (KH_2PO_4) were carried out. In fact, it should be very promising to connect nonlinearity and luminescence of divalent rare earth ions in one material which will be a topic in our future work.

Experimental Section

Synthesis and Crystal Structure Determination. $K_2Mg_2(SCN)_6{\cdot}3H_2O$ was first obtained from a reaction of the binary compounds $MgCl_2{\cdot}xH_2O$ (p. a., Merck) and KSCN (98%, Fluka) in a molar ratio 1:4. The educts were sealed in a quartz glass ampule and heated to 220° followed by slowly cooling using the Bridgman technique. The reaction product contained a large amount of rod shaped colorless crystals of $K_2Mg_2(SCN)_6{\cdot}3H_2O$ up to 1 mm^3 and some KCl powder. The presence of water can be attributed to an incomplete drying of $MgCl_2$. The crystals were slightly moisture sensitive and were handled in a glovebox. Some of them were selected and sealed in glass capillaries (d = 0.1 mm). To check their quality, several exposures were taken on an image plate diffractometer (STOE IPDS), which was also used to collect diffraction data of the best specimen. The structure was solved and refined using the programs SHELXS-86 and SHELXL-93,[18] respectively. Absorption corrections were applied with the aid of the programs X-red and X-shape.[19] The positions of the hydrogen atoms could not be located. Details of the data acquisition and the crystallographic data are summarized in Tables 1−3.

Single phase samples for the investigations described below could be obtained by manual selection of the crystals which were clearly distinguishable from the KCl powder. The purity was checked by X-ray powder diffraction (Stoe and Cie., Stadi P). Unfortunately, we were not successful in preparing single phase samples although we performed several experiments in aqueous solution as well as under hydrothermal conditions. On the other hand, the title compound can be prepared in crystalline form by the reaction of KSCN with $Mg(SCN)_2{\cdot}4H_2O$ at 220 °C together with a not yet defined product. The problem with the synthesis of single phase samples might be due to incongruent melting of the compound. This point will be investigated in the future.

Table 1. Crystallographic Data of $K_2Mg_2(SCN)_6{\cdot}3H_2O$ and Their Determination

lattice constants	a = 885.2(1) pm c = 1732.7(3) pm
molar volume	354.1 cm^3/mol
no. formula units	2
cryst syst	hexagonal
space group	$P6_3cm$ (No. 185)
diffractometer	Stoe IPDS
radiation	Mo Kα (graphite monochrom, λ = 71.07 pm)
temp	293 K
θ range	5° < 2θ < 56°
rotation range; φ-increment	0° < φ < 250°, 2°
index range	$-11 \le h \le 11$ $-11 \le k \le 11$ $-22 \le l \le 22$
no. images	125
exposure time	5 min
detector distance	60 mm
abs correction	numerical after crystal shape optimization[19]
μ	10.04 cm^{-1}
unique reflns	554
with $I_o > 2\sigma(I)$	191
R_{int}	0.0609
structure determinations	SHELXS-86 and SHELXL-93[18]
scattering factors	International Tables, Vol. C[20]
Flack-x	0.3(2)
GOF	0.830
R1; wR2 ($I_o > 2\sigma(I)$)	0.0389; 0.0595
R1; wR2 (all data)	0.1035; 0.0622
CSD no.[a]	413206

[a] Crystallographic data are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (crysdata@FIZ-Karlsruhe.de), on quoting the depository number given in the table.

Table 2. Atomic Positions and Equivalent Displacement Parameters for $K_2Mg_2(SCN)_6{\cdot}3H_2O$

atom	site	x/a	y/b	z/c	$U_{eq}{}^a{\cdot}10^{-1}$/pm^2
K	4b	$^1/_3$	$^2/_3$	0.0511(3)	75(1)
Mg1	2a	0	0	0.0946(4)	36(2)
Mg2	2a	0	0	0.2693(3)	26(2)
S1	6c	0.4458(3)	0.4458(3)	0.9275(3)	68(1)
C1	6c	0.300(1)	0.300(1)	0.9851(7)	40(4)
N1	6c	0.198(1)	0.198(1)	0.0286(5)	43(3)
S2	6c	0.5022(6)	0	0.1749(4)	57.0(8)
C2	6c	0.320(1)	0	0.1800(9)	29(3)
N2	6c	0.190(1)	0	0.1849(7)	33(2)
O	6c	0	0.783(1)	0.3333(5)	72(3)

[a] $U_{eq} = {}^1/_3[U_{33} + 4/3(U_{11} + U_{22} - U_{12})]$.[21]

Table 3. Selected Distances/pm and Angles/deg in $K_2Mg_2(SCN)_6{\cdot}3H_2O$

K−S2 (3×)	333.6(6)	S1−C1	163(1)
K-S1 (3×)	336.9(6)	C1−N1	117(1)
Mg1−N1 (3×)	209(1)	S2−C2	161(1)
Mg1−N2 (3×)	230(1)	C2−N2	116(1)
Mg2−O (3×)	221.9(9)		
Mg2−N2 (3×)	223(1)	N1−C1−S1	178(1)
		N2−C2−S2	179(1)

Second Harmonic Generation. For the measurement of the SHG effect of the powder samples, a comparable equipment

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to the one described in ref 22 was used. Both samples, $K_2Mg_2(SCN)_6 \cdot 3H_2O$ and large crystals of KH_2PO_4 (KDP), were carefully ground. Because the intensity of the frequency doubled radiation depends on the particle size (see below), the size distribution of the powders should be comparable. For this reason, images of both compounds were taken using a scanning electron microscope (SEM XL40, Philips). As a result, both samples show a similar size distribution of 20−200 μm with an average size of about 100 μm. For SHG measurements, thin layers (~ 0.5 mm) of the powders were placed on a microscope slide and fixed with transparent tape.

For excitation, the fundamental radiation of a Q-switched Nd:YAG laser (GCR 11, Spectra Physics, 1064 nm, 8 ns pulse length, 10 Hz) was used. The power was reduced to 100 mJ/pulse to avoid destruction of the sample. To guarantee a constant intensity, a small part of the beam was cut by a beam splitter, and its intensity was observed by a photodiode and monitored by an oscilloscope. The main part of the laser beam was slightly focused (f = 50 cm) on the sample. The resulting frequency doubled radiation was focused on the entrance slit of a 0.27 single monochromator (Spectroscopy Instruments) using a convex lens and detected with a photomultiplier (Hamamatsu, R2949). The signal was preamplified (Stanford, SR445) and measured with a photon counting system (Stanford, SR440).

Vibrational Spectroscopy. Infrared measurements at room temperature from 40 to 4000 cm^{-1} were carried out with a FTIR spectrometer (Bruker, IFS 66v/S). To obtain spectra from 500 to 4000 cm^{-1}, $K_2Mg_2(SCN)_6 \cdot 3H_2O$ was prepared in KBr pellets; for far-IR spectra, polyethylene was used as a pellet material. For the measurements of Raman spectra, additional Raman equipment (Bruker, FRA 106/S) with the 1064 nm emission from a Nd:YAG laser was employed.

Results and Discussion

Crystal Structure. $K_2Mg_2(SCN)_6 \cdot 3H_2O$ crystallizes hexagonally with the noncentrosymmetric space group $P6_3cm$ (Table 1). In the crystal structure, two distinguishable SCN^- ions are present. The distances S−C (163 and 161 pm, Table 3) and C−N (117 and 116 pm) are comparable to those of other rhodanides.[5,17] The angles S−C−N are very close to the ideal 180°.

There exist two different crystallographic positions for Mg^{2+} (Table 2). While Mg1 is surrounded by six nitrogen atoms (3× N1, 3× N2), Mg2 is coordinated by three nitrogen (N2) and three oxygen atoms (Table 3, Figure 1). Both polyhedra can be regarded as slightly distorted octahedra. The distance Mg1−N1 (209 pm) concerning the terminal SCN^- ions and these in $Mg(SCN)_2 \cdot 4H_2O$ (210 pm),[15] where only terminal and no bridging thiocyanate ions exist, match each other closely, while the distance Mg−O (222 pm) is considerably larger compared to those of the tetrahydrate (205 and 213 pm). In $K_2Mg_2(SCN)_6 \cdot 3H_2O$, the Mg1 and Mg2 ions are bridged via three common SCN^- ions (SCN(2)) to dimers, $[Mg_2(SCN(1))_3(SCN(2))_3\ (H_2O)_3]^{2-}$ (Figure 1).

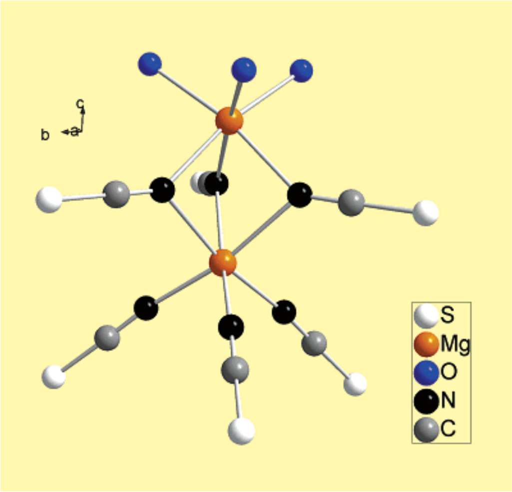

Figure 1. $[Mg_2(SCN)_6(H_2O)_3]^{2-}$ dimers in the crystal structure of $K_2Mg_2(SCN)_6 \cdot 3H_2O$.

In contrast to Mg^{2+}, all K^+ ions are symmetrically equivalent. They are coordinated exclusively by six sulfur atoms (3× S1, 3× S2) in the form of a slightly distorted trigonal prism. The K−S distances are with 334 and 337 pm comparable to those in KSCN (331 and 339 pm[10]), although the potassium ions are coordinated by sulfur and nitrogen atoms in the latter. The $[K(SCN)_6]$ polyhedra are connected with each other via two common edges (1× S1, 1× S2) leading to layers $^{2}_{\infty}[K(SCN)_{6/2}]$ in the (001) plane exhibiting hexagonal K_6S_{12} rings (Figure 2). The sulfur atoms are not located in the plane of the K^+ ions but above (S1) and below (S2) it. The K−S1−C1 angles amount to 74°, which means that the $SCN(1)^-$ anions show in the direction of the K^+ planes. In contrast, SCN(2) moieties are adjusted nearly parallel to the planes (K−S2−N2, 92°; Figure 3).

The $[Mg_2(SCN)_6(H_2O)_3]^{2-}$ dimers are arranged in the K_6S_{12} plane in such a way that the Mg1 ions are connected to the N1 and N2 atoms and, therefore, are located in the planes. In contrast, the Mg2 ions which are connected to the N2 atoms are outside of the planes. The layers are arranged with an equal alignment along [001], so that the polar symmetry can be easily observed (Figure 3). The layers are connected mainly via S···H hydrogen bonds. While the S−O distances (S1−O, 342 pm) between the layers indicate strong sulfur hydrogen bonding, the respective nitrogen bonds (N1−O, 385 pm) are rather weak. On the other hand, the hydrogen bonds inside one layer are due to N···H bonding (S2−O, 371 pm; N2−O, 314 pm). Strong hydrogen bonding is also indicated by the vibrational spectra (see below). The respective layers cannot be depicted by translational symmetry operations, but an additional rotation of 60° of the $[Mg_2(SCN)_6(H_2O)_3]^{2-}$ dimers must be performed (Figure 2). Because of this, two layers are included in the elementary cell.

SHG Effect. Bright green radiation can be observed by eye if a powder sample of $K_2Mg_2(SCN)_6 \cdot 3H_2O$ is irradiated by the IR beam of the Nd:YAG laser. Because of this high efficiency of the SHG effect, it can be assumed that the title compound is phase-matchable. The resulting spectrum shows one strong peak with a maximum at 532 nm (18797 cm^{-1}) as can be expected for the frequency doubling of the 1064 nm (9398.5 cm^{-1}) radiation of the Nd:YAG laser. The second harmonic intensity depends nearly quadratically on those of the fundamental beam (1.85 ± 0.2), which can be taken as proof that the green radiation is indeed due to second harmonic generation.

For estimation of the intensity of the effect, an identical measurement with KDP was carried out. KDP

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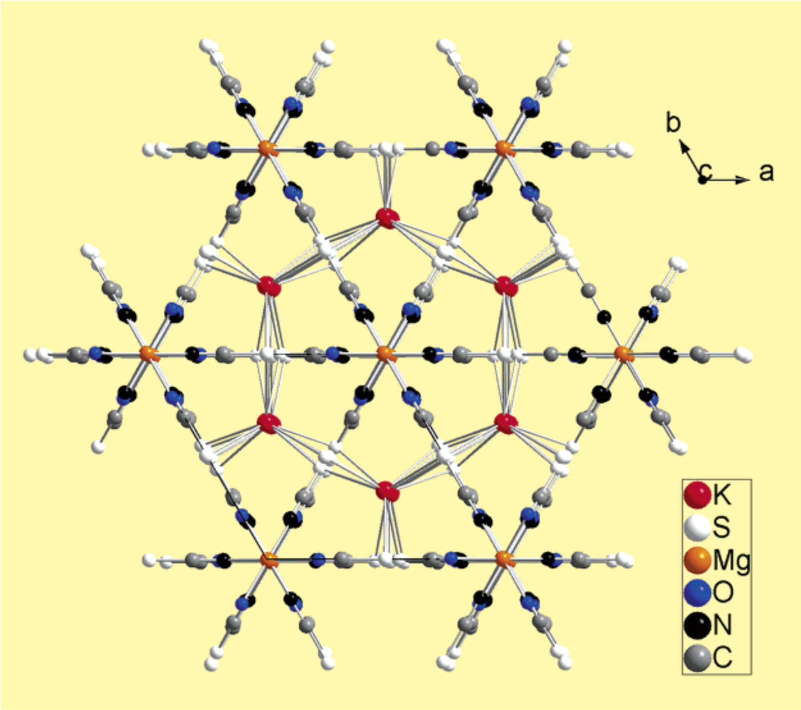

Figure 2. Projection of the crystal structure of $K_2Mg_2(SCN)_6{\cdot}3H_2O$ on (001).

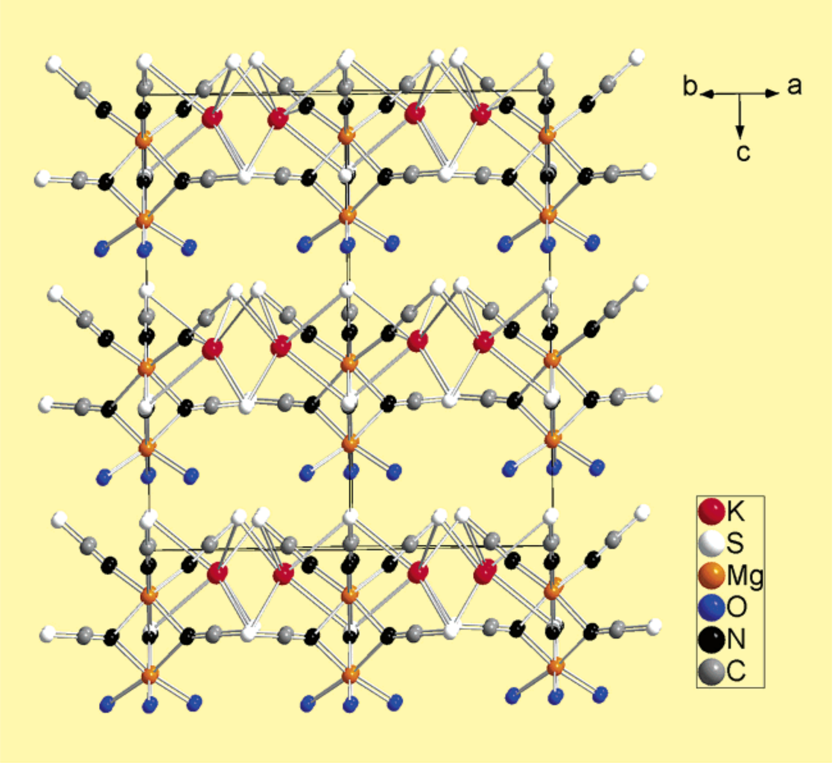

Figure 3. Perspective view of the crystal structure of $K_2Mg_2(SCN)_6{\cdot}3H_2O$ along [110]. The respective layers are exclusively connected by hydrogen bonds.

(space group $I\bar{4}2d$[23]) is a well-known noncentrosymmetric material with a large SHG effect (type I, $d_{\mathrm{eff}} = 0.2553$; type II, $d_{\mathrm{eff}} = 0.3464$ for $\lambda = 1064$ nm[24]) which is used for frequency doubling of laser radiation. In this case, a similar spectrum was obtained, but the intensity of the peak is larger. By integrating the peaks, it can be concluded that the intensity for $K_2Mg_2(SCN)_6{\cdot}3H_2O$ is about 40% of that for KDP. However, this is only a qualitative statement. For more exact measurements, powders should be graded by using appropriate sieves.[22] On the other hand, the error due to the use of powders with a large size distribution should be rather small. In the case of not phase-matchable compounds, the intensity of frequency doubling depends very strongly on the averaged particle size *r* where a maximum is

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Table 4. Frequencies/cm^{-1} and Assignments of the IR and Raman Bands of $K_2Mg_2(SCN)_6\cdot 3H_2O$

IR	Raman	vibration	position in free molecule
56	58		
76	77		
	91	outer vibrations	
117	112		
150	156		
174	176		
	205		
215	216		
322	326		
382	382		
463		$\rho_w(H_2O)$?	
473		$\delta(SCN)$	470(Π)[25]
486	484		
505	506		
542		$\rho(H_2O)$	
608			
719			
746			
789	774	$\nu(SC)$	743(Σ^+)[25]
800	801		
827	819		
856		$\delta(MgOH)$	
881			
968	968	$2\delta(SCN)$	
	980		
	1094	?	
1626		$\delta(H_2O)$	1595(A_1)[26]
2008	2008		
2048	2046		2066(Σ^+)[25]
	2062	$\nu(CN)$	
2091	2089		
2106	2106		
	3171	$\nu_s(H_2O)$	3657(A_1)[26]
3269	3269		
3435		$\nu_{as}(H_2O)$	3756(B_2)[26]
3678			

reached if the size is closed to the average coherent length l_c. In contrast, for phase-matchable materials the intensity increases with increasing particle sizes for $r < l_c$ but stays nearly constant for $r > l_c$.[22] In the present case, the use of ungraded powder samples should be satisfactory for qualitative statements because of the assumption of phase-matchability (see above). Furthermore, the intensity depends on the angle between the detector and the direction of incident light beam θ ($I(\theta, \Phi) = I_0 \cos \theta^{22}$). Thus, for quantitative measurements a parabolic reflector or an integrating sphere should be used for the complete detection of the frequency doubled radiation.

Vibrational Energies. Infrared and Raman spectra are depicted in Figures 4 and 5, and the energies of the transitions and their assignments are summarized in Table 4. Because the most striking features are due to transitions of the molecular units of the compounds, the spectra are comparable to those of $Ca(SCN)_2\cdot 2H_2O$.[6] $K_2Mg_2(SCN)_6\cdot 3H_2O$ can be described with the factor group C_{6v}, and therefore, the optical phonon modes belong to the irreducible representations $\Gamma_v = 19A_1 + 11A_2 + 20B_1 + 11B_2 + 30E_1 + 24E_2$ if one assumes that the hydrogen ions occupy a general site. The A_1 and E_1 modes are IR active while the modes belonging to A_1, E_1, and E_2 can be observed in Raman spectra. As a result, 49 bands are observable in the IR spectrum at maximum, but only 29 bands are detected (Table 4). The reason for this reduction is the low intensity of some bands and the small difference in energy to be resolved. The same is true for Raman spectra, where only 23 of the possible 73 transitions are recorded.

The transitions below 400 cm^{-1} are due to outer vibrations of the cation−ligand bonds. In $[Mg(H_2O)_6]^{2+}$ complexes, the $\nu(MgO)$ stretching vibrations are at 310 cm^{-1},[27] so that the peaks at 322 (IR) and 326 (Raman) cm^{-1} may be assigned to this mode. The bands at higher energy originate mostly from vibrations of the molecular units, e.g., SCN^- ions and H_2O molecules. The increasing numbers of these transitions can be due to the removal of degeneracy due to the lower symmetry in the solid and/or to factor group multiplication. The peak in the Raman spectrum at 1094 cm^{-1} cannot be assigned.

The energies of the thiocyanate bending and stretching modes depend on the bonding conditions. In the case of N bonding, $\nu(SC)$ and $\delta(SCN)$ are located at lower frequencies than in the free ion. The opposite is true

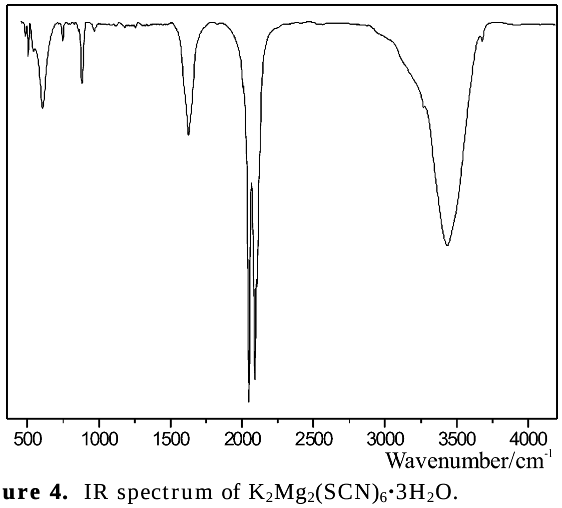

Figure 4. IR spectrum of $K_2Mg_2(SCN)_6\cdot 3H_2O$.

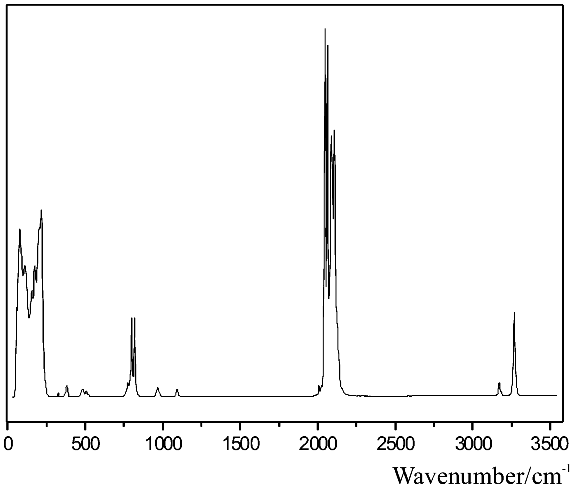

Figure 5. Raman spectrum of $K_2Mg_2(SCN)_6\cdot 3H_2O$.

for S bonding.[28] In the present case, the positions of these modes are comparable to these of free SCN^- because of the bridging of the thiocyanate unit. In contrast to $M(SCN)_2$ (M = Eu, Sr, Ba)[5] but similar to $Ca(SCN)_2$ and $Ca(SCN)_2{\cdot}2H_2O$,[6] the modes assigned to δ(SCN) could be observed in both IR and Raman spectra.

The positions and the shape of the modes belonging to the water molecules display the existence of hydrogen bonds.[29] Both stretching vibrations are shifted to lower energy compared to these of the free molecule, and the energy of $\delta(H_2O)$ is slightly increased. Additionally, the stretching modes appear as very broad bands in the IR spectrum. In contrast to other hydrates, like $Ca(SCN)_2{\cdot}2H_2O$,[6] the $\nu_s(H_2O)$ transitions could be detected in the Raman measurements with remarkable intensity (Figure 5). Besides the bending and stretching vibrations of the water molecules, some librational modes below 800 cm^{-1} should exist.[27] These are the wagging mode $\rho_w(H_2O)$, the rocking mode $\rho_r(H_2O)$, and the twisting mode $\rho_t(H_2O)$. In $[Mg(H_2O)_6]^{2+}$, $\rho_w(H_2O)$ is located at 460 cm^{-1}, and therefore, one of the transitions in this region may be assigned to this mode rather to δ(SCN) in the present case. The other two librational modes arise at slightly higher energy, so that the two transitions at 542 and 608 cm^{-1}, respectively, are probably due to these vibrations.

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Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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