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High-Resolution ^{113}Cd MAS NMR Investigation of Structure and Bonding in Cadmium Thiocyanate Coordination Compounds. Distance Dependence of Cadmium–Nitrogen Indirect Spin–Spin Coupling Constants[†]

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A number of cadmium thiocyanate complexes of varying stoichiometry (1:2, 1:3, 1:4) have been prepared and investigated by solid-state ^{113}Cd MAS NMR spectroscopy. The application of this technique in characterizing the various modes of linkage isomerism exhibited by the ambidentate thiocyanate ligand is discussed in detail. The ^{113}Cd isotropic chemical shifts and chemical shift anisotropies provide information concerning the coordination number of cadmium in these complexes. For the octahedral complexes, the ^{113}Cd isotropic chemical shifts span a range of 213 ppm with the Cd(*N*CS)$_6$ fragment being most shielded ($\delta_{iso} = 130.0$ ppm) and the Cd(*S*CN)$_6$ fragment being least shielded ($\delta_{iso} = 342.9$ ppm). Each distinct cadmium site in the cadmium thiocyanates exhibits multiplets that result from ^{113}Cd,^{14}N spin–spin coupling. Analysis of these multiplets reveals the number of nitrogen atoms attached to cadmium. The magnitudes of the indirect ^{113}Cd,^{14}N spin–spin coupling constants in these complexes vary from 37 to 178 Hz and appear to be related to the cadmium–nitrogen separation.

Introduction

The coordination chemistry of ligands possessing two different atoms capable of coordinating to metal ions has long been a subject of interest to both the synthetic and the theoretical chemist. Investigations demonstrating the utility of these ambidentate ligands as sensitive chemical probes of electronic or steric changes have resulted in numerous publications.[1] Examples of thiocyanate linkage isomerism have dominated this area and have revealed a variety of different coordination modes. In addition to the terminal *S*- and *N*-bonding modes (thiocyanato and isothiocyanato, respectively), five different bridging modes (–SCN–, =SCN, SCN=, =SCN–, ≡SCN) have been established by single-crystal X-ray diffraction studies.[1f] Besides X-ray diffraction techniques, infrared and Raman spectroscopy have also been applied to characterize the different modes of bonding. However, the interpretation of infrared data is not always reliable.[1c,d]

Although multinuclear NMR spectroscopy of solutions is one of the most important techniques for structural characterization, its successful application to metal thiocyanate complexes has been limited to a few cases. Most of these studies have utilized nuclei present within the thiocyanate ligand itself (^{13}C, ^{14}N, ^{15}N)[2-9] or more remote nuclei in the coordination sphere of the central metal (*e.g.*, ^{31}P).[10] Only a few investigations have reported the direct NMR detection of the coordinated metal nucleus (^{93}Nb, ^{103}Rh, ^{119}Sn, ^{195}Pt).[11-13] The major problem with solution NMR studies is that the structural integrity of these complexes, as established by single-crystal X-ray diffraction, is lost in solution. In addition, the interpretation of the NMR spectra is often complicated by rapid ligand–metal exchange. Furthermore, efficient ^{14}N relaxation via the quadrupolar mechanism[14] generally results in self-decoupling of the ^{14}N nucleus, precluding the direct observation of indirect spin–spin coupling constants, *J*, between NMR-active metal nuclei and ^{14}N. The observation of J(M,^{14}N) is important because the magnitude of *J* indicates the mode of bonding and the multiplicity in NMR spectra of the metal nucleus provides information on the number of nitrogen atoms directly bonded to the metal.[13,15]

Among thiocyanate coordination compounds, the complexes of cadmium are of particular interest. First, the Cd^{2+} ion is an acid of intermediate softness[16] forming many different linkage isomers with the thiocyanate ligand. Second, the two spin-$^1/_2$ isotopes of cadmium, ^{111}Cd (12.8%) and ^{113}Cd (12.3%), allow one to use metal NMR to study the metal center directly.[17] In addition, the environment provided by the thiocyanate ligands might serve as a model for other nitrogen and sulfur donor ligands found in bio-inorganic compounds.[18]

In a preliminary solid-state ^{113}Cd NMR study of (N-*n*-Pr$_4$)[Cd(SCN)$_3$] we were able to demonstrate that the aforementioned problems of solution NMR studies can be overcome in the solid

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[†] Dedicated to Professor Ekkehard Lindner on the occasion of his 60th birthday.

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state.[19] Specifically, it was possible to measure distinctive ^{113}Cd,^{14}N spin–spin coupling constants to each of the unique N-bonded thiocyanate ligands established by X-ray diffraction techniques. Here we extend our study to a series of cadmium thiocyanate complexes of varying stoichiometry. Since most of these complexes have been previously characterized by X-ray diffraction, they provide one with an ideal opportunity to examine the relationship between the ^{113}Cd NMR parameters and molecular structure. It is important to emphasize that none of the complexes investigated here maintain their solid-state structure in solution.

Experimental Section

All compounds were prepared according to literature methods. $Cd(SCN)_2$, **1**, was prepared from cadmium sulfate and barium thiocyanate in water.[20] $Cd(SCN)_2 \cdot NH_3$, **2**, was formed from the reaction of freshly prepared cadmium hydroxide with ammonium thiocyanate in water.[20] $Cd(SCN)_2 \cdot C_6H_{12}N_4 \cdot 2H_2O$, **3**,[21] $Na[Cd(SCN)_3] \cdot 3H_2O$, **4**,[20] $(NMe_4)[Cd(SCN)_3]$, **5**,[22] $(NEt_4)[Cd(SCN)_3]$, **6**,[23] $Rb[Cd(SCN)_3]$, **7**, $Cs[Cd(SCN)_3]$, **8**,[24] $(NMe_4)_2[Cd(SCN)_4]$, **9**,[22] $K_2[Cd(SCN)_4] \cdot 2H_2O$, **10**,[20] and $K_2[Cd(CN)_2(SCN)_2] \cdot 4H_2O$, **11**,[25] were prepared by the reaction of **1** with stoichiometric amounts of the appropriate monovalent thiocyanate or cyanide salt or amine in water (**3**, **4**, **7**, **8**, **10**, **11**) or methanol (**5**, **6**, **9**).

All solid-state ^{113}Cd NMR spectra were obtained on a Bruker MSL 200 spectrometer ($B_0 = 4.7$ T) operating at 200.13 MHz for ^{1}H and 44.38 MHz for ^{113}Cd, using a Bruker double-bearing MAS probe. The solid samples were ground to fine powders and packed into zirconium dioxide rotors (7-mm o.d.). The ^{113}Cd CP/MAS NMR spectra of compounds **2**–**6** and **9**–**11** were acquired after cross-polarization under the condition of the Hartmann–Hahn match and with high-power proton decoupling. Typically, ^{1}H $\pi/2$ pulse widths of 4.0 μs, contact times of 4 ms, and recycle delays of 8–20 s were employed. For the complexes lacking ^{1}H nuclei, **1**, **7**, and **8**, single-pulse experiments with recycle delays of 30–100 s were used. Cadmium-113 chemical shifts were referenced by setting the peak of $Cd(NO_3)_2 \cdot 4H_2O$ to −100 ppm.[26] The free induction decays were processed using a slight Gaussian resolution enhancement.

Theoretical Background

The MAS NMR spectrum of a spin-$^1/_2$ nucleus, I, which is spin-spin coupled to a nucleus with $S > {}^1/_2$ might be expected to exhibit a multiplet consisting of $2S + 1$ peaks of equal intensity and equally separated by the indirect spin–spin coupling constant, J_{iso}. However, if the electric-field gradient (EFG) at the quadrupolar nucleus, S, is nonzero, the S spin Zeeman states will be perturbed. As a result of this perturbation, the I and S spins are not quantized along the same axis and magic-angle spinning (MAS) fails to remove anisotropic I,S spin–spin interactions, *i.e.*, direct dipolar and/or anisotropic indirect coupling. Thus, the perturbation of the S spin states is reflected in the I spin MAS NMR spectrum and the $2S + 1$ lines are shifted, broadened, and/or show additional fine structure due to this residual dipolar coupling.

The theoretical analysis of an I,S spin-pair under the condition of MAS has been outlined in the literature. Most of the earlier treatments used time-consuming calculations involving full S-spin Hamiltonian diagonalization and space-partitioning procedures.[27] However, Hexem *et al.*[27d] have shown that if the quadrupolar interaction is small compared to the Zeeman interaction, then first-order perturbation theory adequately reproduces the experimental spectra. Recently, Olivieri and co-workers expanded and generalized the first-order perturbation approach to treat systems with nonaxially symmetric EFG tensors,[28] indirect spin–spin coupling,[29] and $S \geq 1$.[30] Detailed calculations of the line shapes in ^{13}C MAS NMR spectra due to ^{13}C,^{14}N spin-pairs using this first-order approach have been published.[31] If the contribution of the residual dipolar coupling to the actual line shape is small, further simplification is possible.[32] Under these conditions, the resonance frequencies in the MAS NMR spectrum of a spin-$^1/_2$ nucleus coupled to a quadrupolar spin-S nucleus are given by[30]

$$\nu_m = \nu_{iso} - m|J| - \frac{S(S+1) - 3m^2}{S(2S-1)}d \qquad (1)$$

where ν_{iso} is the frequency of the uncoupled I nucleus and m is the z-component of the angular momentum of the $|m\rangle$ state of nucleus S, *i.e.*, $m = S, S-1, \ldots, -S$. The residual dipolar coupling, d, is given by

$$d = -\frac{3\chi D}{20Z}(3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos 2\alpha^D) \qquad (2)$$

with the quadrupolar coupling constant, $\chi = e^2Qq_{zz}/h$, the asymmetry parameter of the EFG tensor, $\eta = (q_{xx} - q_{yy})/q_{zz}$, with principal values $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$, and the Larmor frequency, $Z = \gamma_S B_0/2\pi$, of the S nucleus. The dipolar coupling constant D is given by

$$D = \left(\frac{\mu_0}{4\pi}\right)\frac{\gamma_I\gamma_S}{r_{IS}^{\,3}}\left(\frac{h}{2\pi}\right) \qquad (3)$$

and the azimuthal and polar angles, α^D and β^D, define the orientation of the dipolar vector, r_{IS}, with respect to the principal axis system of the EFG tensor. In systems where anisotropy in **J** has to be considered, the parameter D in eq 2 is replaced by an effective dipolar coupling constant $D' = D - \Delta J/3$, with $\Delta J = J_{\parallel} - J_{\perp}$ and $J = (J_{\parallel} + 2J_{\perp})/3$, assuming axial symmetry for **J** and $J_{\parallel}$ parallel to r_{IS}. All calculated spectra in the present study were generated using eq 1. The resulting "stick" spectra were convoluted with a Gaussian/Lorentzian peak of appropriate mixture and line width. A computer program for IBM-compatible computers which calculates these spectra is available from the authors on request.

Results and Discussion

Analysis of ^{113}Cd MAS NMR Spectra. Cadmium-113 chemical shifts and values of $^1J(^{113}Cd,^{14}N)$ and d obtained from analysis of the ^{113}Cd MAS NMR spectra are given in Table 1, together with literature values of r_{CdN}. Before discussing our results in

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Table 1. Coordination of Cadmium, Isotropic ^{113}Cd NMR Chemical Shifts, ^{113}Cd,^{14}N Indirect Spin–Spin Coupling Constants, Residual Dipolar Couplings, and Cd–N Separations Observed for Cadmium Thiocyanate Complexes

compd	coord	δ_{iso} (ppm)	$^1J(^{113}\mathrm{Cd},\,^{14}\mathrm{N})$ (Hz)	d (Hz)	$r_{\mathrm{CdN}}{}^{a}$ (Å)
$Cd(SCN)_2$, **1**	CdN_2S_4	280.5	125 ± 4	5.0 ± 2.0	2.24
			106 ± 4	3.5 ± 2.0	2.24
$Cd(SCN)_2 \cdot NH_3$, **2**	CdN_2S_4	288.8	37 ± 1	1.9 ± 0.3	
$Cd(SCN)_2 \cdot C_6H_{12}N_4 \cdot 2H_2O$, **3**	CdN_3S_2O	210.8	95 ± 2	6.5 ± 0.5	2.399
			80 ± 2	5.0 ± 0.5	2.299
			80 ± 2	5.0 ± 0.5	2.319
$Na[Cd(SCN)_3] \cdot 3H_2O$, **4**	CdN_3S_3	217.1	96 ± 1	4.2 ± 0.1	
$(NMe_4)[Cd(SCN)_3]$, **5**	CdN_3S_3	192.3	87 ± 8	5.0 ± 2.0	2.280
			65 ± 8	4.0 ± 2.0	2.344
			57 ± 8	4.0 ± 2.0	2.378
$(NEt_4)[Cd(SCN)_3]$, **6**	CdN_3S_3	187.3	80 ± 8	5.0 ± 3.0	2.253
			68 ± 8	4.0 ± 3.0	2 at 2.336
$Rb[Cd(SCN)_3]$, **7**	CdN_2S_4	275.8	59 ± 3	4.0 ± 2.0	2 at 2.320
	CdN_4S_2	223.3	85 ± 10	5.0 ± 2.0	2 at 2.282
			68 ± 10	5.0 ± 2.0	2 at 2.307
$Cs[Cd(SCN)_3]$, **8**	CdS_6	342.9	*b*		
	CdN_6	130.0	*c*		2 at 2.281
					2 at 2.304
					2 at 2.409
$(NMe_4)_2[Cd(SCN)_4]$, **9**	CdN_4S_2	175.6	117 ± 2	6.0 ± 1.0	2 at 2.269
			66 ± 2	4.5 ± 1.0	2 at 2.357
$K_2[Cd(SCN)_4] \cdot 2H_2O$, **10**	CdN_2S_4	296.0	42 ± 4	1.0 ± 3.0	2.45
$K_2[Cd(CN)_2(SCN)_2] \cdot 4H_2O$, **11**	*d*	204.6	135 ± 3	5.0 ± 1.0	
$(N\mathit{n}Pr_4)[Cd(SCN)_3]$, **12**^{e}	CdN_3S_2	310.0	178 ± 2	3.8 ± 0.5	2.163
			50 ± 2	4.7 ± 0.5	2.338
			38 ± 2	4.2 ± 0.5	2.363

[a] For references, see text. [b] Line width 80 Hz. [c] Line width 480 Hz. [d] See discussion. [e] Reference 19.

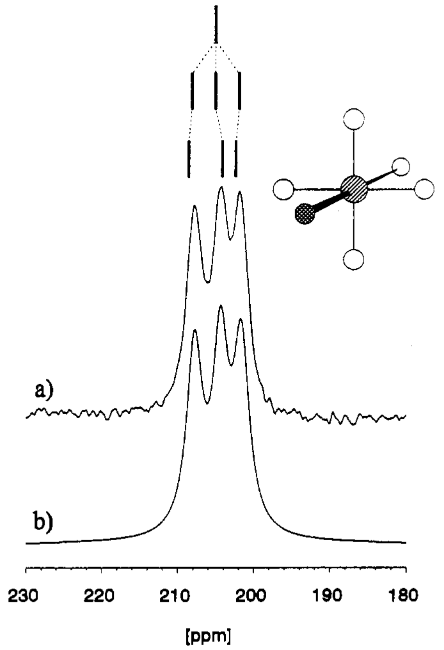

Figure 1. Isotropic region of the ^{113}Cd CP/MAS NMR spectrum of $K_2[Cd(CN)_2(SCN)_2] \cdot 4H_2O$, **11**: (a) experimental spectrum, MAS rate 2520 Hz, recycle delay 20 s, contact time 8 ms, 972 scans; (b) calculated spectrum. The scheme on top illustrates the effect of spin–spin coupling of ^{113}Cd with one ^{14}N nucleus: the indirect spin–spin coupling results in three equidistant peaks, while the residual dipolar coupling causes shifts of the individual transitions.

detail, it is instructive to consider a simple example. Figure 1a shows the experimental ^{113}Cd CP/MAS NMR spectrum of $K_2[Cd(CN)_2(SCN)_2] \cdot 4H_2O$, **11**. From eq 1, it is clear that the asymmetric multiplet is fully described by two parameters, the indirect spin–spin coupling constant, J, and the residual dipolar coupling, d. The splitting between the two high-frequency peaks is given by $J + 3d$, while the other splitting corresponds to $J - 3d$. This convenient approach can be extended to the analysis of systems where more than one spin-S nucleus is present, since each of the three lines will be split successively into new asymmetric triplets for each additional spin-S nucleus.[19,33] Hence, the multiplets arising from spin–spin interactions with quadrupolar nuclei can be analyzed in a straightforward manner to yield values of J and d.

Several features of these spectra are worth noting. First, in systems where the first-order treatment is valid, no information about the sign of J can be obtained.[27d,32] In the case of cadmium pyridine adducts, the absolute sign of $^1J(^{113}\mathrm{Cd},^{15}\mathrm{N})$ was determined to be positive;[18c] hence, negative signs for $^1J(^{113}\mathrm{Cd},^{14}\mathrm{N})$ are anticipated. As well, the sign of D has no effect on the appearance of the spectrum;[31b,34] only the sign of χ and of the orientational dependent term in eq 2 affect the sign of d.

In the discussion which follows it is assumed that nitrogen interacting with cadmium over three bonds leads only to line broadening, not to observable splittings (*i.e.*, $^3J(^{113}\mathrm{Cd},^{14}\mathrm{N}) < \Delta\nu_{1/2}$). This assumption is based on a comparison with results from NMR studies in solution, involving ^{15}N-labeled thiocyanate ligands.[35–37]

Finally, it should be noted that, in principle, an ambiguity could exist in analyzing spectra of the type shown in Figure 1 which is related to the relative magnitudes of J and d. If $|J| > |3d|$, the inner peak of the triplet is associated with the $m = 0$ spin state of ^{14}N, while for $|J| < |3d|$, one of the outer peaks is associated with this spin state. Hence, three solutions are possible, dependent on the assignment of the peak associated with the $m = 0$ spin state. This ambiguity can be resolved by obtaining spectra at a different magnetic field strength or by isotopic labeling with ^{15}N. Furthermore, since ^{14}N quadrupolar coupling constants for several

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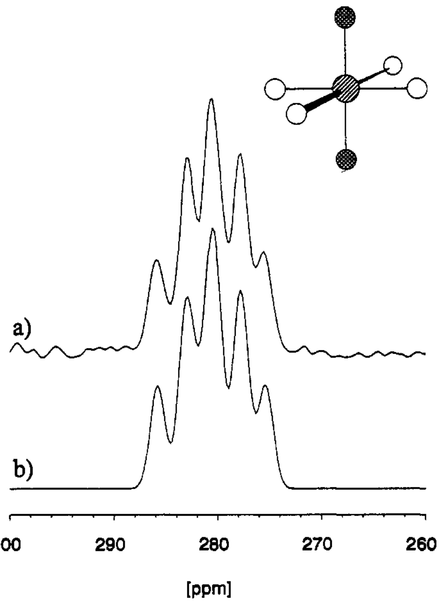

Figure 2. Isotropic region of the ^{113}Cd MAS NMR spectrum of Cd$(SCN)_2$, **1**, showing spin–spin coupling of ^{113}Cd with two ^{14}N nuclei: (a) experimental spectrum obtained after single-pulse excitation, MAS spinning rate 3264 Hz, recycle delay 60 s, 702 scans; (b) calculated spectrum.

thiocyanate salts and complexes are known,[38] the magnitude of *d* can be estimated. Typically, χ is largest, 3–3.5 MHz, if the nitrogen of the thiocyanate moiety is not coordinated, while for *N*-bonded thiocyanate ligands smaller values of χ, *i.e.*, <1.6 MHz, can be found.[38] Taking 2.0 MHz as an upper limit of χ for the *N*-bonded thiocyanate ligand, and r_{CdN} = 2.3 Å as an average Cd–N bond distance, it is straightforward to show that the maximum magnitude of *d* is 6–7 Hz, far smaller than the values of *J* obtained in the present study (Table 1); hence, the inner peak of the "triplet" is associated with $m = 0$.

Since the coordination mode of the thiocyanate ligand changes with the cadmium:thiocyanate stoichiometry, the compounds investigated in the present study may be divided into three groups: 1:2, 1:3, and 1:4 complexes. In order to achieve octahedral coordination, a decrease in the Cd:SCN ratio causes increasing contributions from bridging modes. Below, we shall first discuss the ^{113}Cd MAS NMR spectra of the compounds under investigation in terms of their crystal structures, where available, and then attempt to derive some general conclusions from the data at hand.

1:2 Complexes. The first group, with a cadmium:thiocyanate ratio of 1:2, includes cadmium thiocyanate itself, $Cd(SCN)_2$, **1**, and cadmium thiocyanate with an additional molecule of ammonia, $Cd(SCN)_2{\cdot}NH_3$, **2**, or hexamethylenetetramine, $Cd(SCN)_2{\cdot}C_6H_{12}N_4{\cdot}2H_2O$, **3**. Compounds **1** and **2** were described in the first thorough study of cadmium thiocyanates near the turn of the century.[20] The ^{113}Cd MAS NMR spectrum of $Cd(SCN)_2$, **1**, is shown in Figure 2. The multiplet consists of five peaks, indicative of coupling of ^{113}Cd with two ^{14}N nuclei. The best agreement between the experimental and the calculated spectrum was achieved by introducing two slightly different ^{14}N nuclei with different values of *J*, 125 and 106 Hz, and *d*, 5.0 and 3.5 Hz (Table 1). This is consistent with the structure of **1** determined by X-ray crystallography,[39] which indicates that cadmium is surrounded octahedrally by four sulfur and two slightly nonequivalent nitrogen atoms. Due to the low Cd:SCN ratio, each thiocyanate ligand is bonded to three cadmium atoms, with the sulfur bridging two cadmium atoms while the nitrogen is attached to a third cadmium center. As a result of this unusual bonding mode of the thiocyanate ligand, the structure of **1** is a dense network, and of all other octahedral complexes investigated here, the coupling constants $^1J(^{113}Cd,^{14}N)$ exhibit the greatest magnitudes. The line width of the individual peaks of the multiplet is relatively high (about 70 Hz). For aqueous solutions of $Cd(SCN)_2$, δ_{iso} = 60 ppm, indicative of a completely different structure from that in the solid state.[17d]

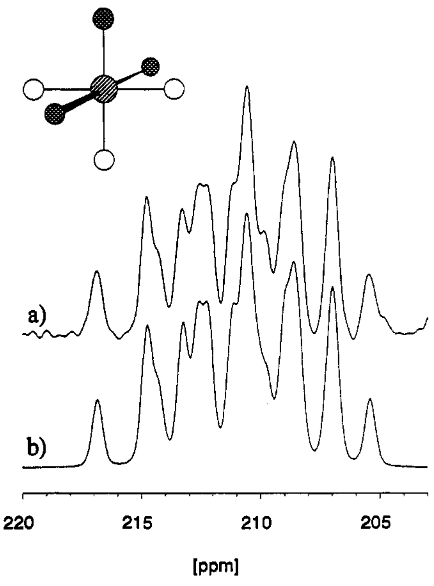

Figure 3. Isotropic region of the ^{113}Cd CP/MAS NMR spectrum of $Cd(SCN)_2{\cdot}C_6H_{12}N_4{\cdot}2H_2O$, **3**, showing spin–spin coupling of ^{113}Cd with three ^{14}N nuclei: (a) experimental spectrum obtained at a MAS spinning rate of 2980 Hz, recycle delay 20 s, contact time 5 ms, 452 scans; (b) calculated spectrum.

The ^{113}Cd CP/MAS NMR spectrum of $Cd(SCN)_2{\cdot}NH_3$, **2**, is similar to that shown for **1** in Figure 2, except for the much smaller values of $^1J(^{113}Cd,^{14}N)$ (Table 1). Both nitrogen atoms are equivalent within experimental error. Because the crystal structure of **2** is unknown, information concerning the position of the NH_3 group is not available. The ^{113}Cd chemical shift of **2** is similar to the value observed for **1**, while the ^{113}Cd chemical shift anisotropy of **2** ($\delta_{11} \approx 370$, $\delta_{22} \approx 270$, $\delta_{33} \approx 210$ ppm) is slightly larger and less symmetric than that of **1** ($\delta_{11} \approx 320$, $\delta_{22} \approx \delta_{33} \approx 240$ ppm). Also, the peaks in the ^{113}Cd MAS NMR spectrum of **2** are narrower (ca. 25 Hz). Taking these facts together, there is no indication for Cd–NH_3 coordination. On the basis of the significantly smaller values of $^1J(^{113}Cd,^{14}N)$, 37 Hz, we assumed that the dense network described for **1** has opened in **2**, with the NH_3 positioned in cavities within this framework.

While there is no evidence for coordination of NH_3 toward cadmium available from the ^{113}Cd CP/MAS NMR spectrum of **2**, the spectrum observed for $Cd(SCN)_2{\cdot}C_6H_{12}N_4{\cdot}2H_2O$, **3**, is more complex (Figure 3). According to the crystal structure, cadmium is coordinated in an octahedral fashion with four bridging thiocyanate ligands in the equatorial plane, two *N*-bonded ligands trans to one another, and similarly two trans *S*-bonded groups. The two axial sites are occupied by hexamethylenetetramine and water. In agreement with this structure, the multiplet observed in the ^{113}Cd CP/MAS NMR spectrum indicates spin–spin coupling of cadmium with three nitrogen nuclei (Table 1). Although the diffraction results indicate that the Cd–N bond distances involving the two thiocyanate ligands are slightly different,[21] two of the ^{14}N nuclei contributing to the multiplet shown in Figure 3 are equivalent within experimental error. The unique values of *J* and *d* are assigned to the hexamethylenetetramine ligand, particularly since the value of *d* is relatively high, compared with the results for **1**–**11** (Table 1). Assuming an axially symmetric ^{14}N EFG tensor ($\eta = 0$) and $\beta^D = 0°$, χ is estimated to be −2.2 MHz, which appears to be a reasonable

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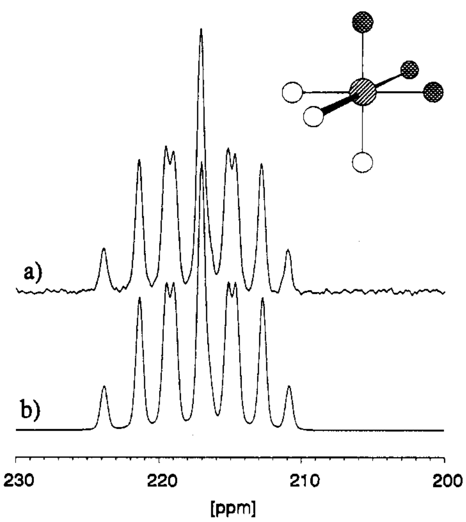

Figure 4. Isotropic region of the ^{113}Cd CP/MAS NMR spectrum of Na[Cd(SCN)$_3$]·3H$_2$O, **4**, showing spin–spin coupling of ^{113}Cd with three equivalent ^{14}N nuclei: (a) experimental spectrum obtained at a MAS spinning rate of 3100 Hz, recycle delay 8 s, contact time 12 ms, 1815 scans; (b) calculated spectrum.

value for a coordinated amine ligand.[40] Note that the three values of $J(^{113}\mathrm{Cd},^{14}\mathrm{N})$ in **3** differ by less than 20%, with the value involving the amine ligand being the largest. This appears to be inconsistent with arguments based on the Fermi contact mechanism where it is generally found that J increases with the "s-character".[37] In the case of **3**, $J(^{113}\mathrm{Cd},^{14}\mathrm{N})$ appears largest for the amine nitrogen which has the largest Cd–N separation. Possibly, other coupling mechanisms can play a role in the transmission of spin information through the Cd,N bond, as experimental results have shown for $^2J(^{199}\mathrm{Hg},^{14}\mathrm{N})$.[41]

1:3 Complexes. The second group of cadmium thiocyanate coordination compounds, with a cadmium:thiocyanate ratio of 1:3 and a monovalent cation present, includes the compounds Na[Cd(SCN)$_3$]·3H$_2$O, **4**, (NMe$_4$)[Cd(SCN)$_3$], **5**, (NEt$_4$)[Cd(SCN)$_3$], **6**, Rb[Cd(SCN)$_3$], **7**, and Cs[Cd(SCN)$_3$], **8**. They have the general formula AMX$_3$ and as such may be considered as related to perovskites,[42] a class of compounds well-known for their structural diversity. Thus, they may exhibit a three-dimensional network, two-dimensional planes, or one-dimensional chains of linked octahedra, MX$_6$. All three types of connectivities are found in the compounds studied here.

The sodium salt Na[Cd(SCN)$_3$]·3H$_2$O, **4**, is one of the first cadmium thiocyanate complexes described in the literature;[20] however, the crystal structure of this compound is unavailble. The ^{113}Cd CP/MAS spectrum of this complex (Figure 4) contains detailed information. At first sight, the experimental multiplet shown in Figure 4 appears symmetrical with no indication of a breakdown of the high-field approximation for ^{14}N (*i.e.*, it appears that d = 0 Hz). A closer inspection, however, reveals that the separation between the peak at highest frequency and the adjacent inner peak is slightly greater than the corresponding separation in the low-frequency region of the spectrum. As well, it can be shown that the splittings of the peaks flanking the central peak equals $6d$. The calculated spectrum shown in Figure 4 has been generated by introducing spin-spin interactions of cadmium with three equivalent ^{14}N nuclei and is in excellent agreement with the experimental spectrum. Further evidence for the equivalence of the thiocyanate groups stems from the ^{13}C CP/MAS spectrum of **4**, which indicates only one distinct carbon site. This requires that the nitrogen atoms are coordinated to the cadmium in a facial manner, a favored mode also adopted by **5** and **6**, and that the thiocyanate ligands are *S,N*-bridging. Note the similarity between the multiplet pattern due to three equivalent ^{14}N nuclei (Figure 4) and that for which one of the three ^{14}N nuclei is unique (Figure 3). The ^{113}Cd MAS NMR line width of 20 Hz for **4** is relatively narrow.

Due to the large number of nitrogen atoms coordinated to cadmium in compounds **5–8**, 3–6, the ^{113}Cd MAS NMR spectra exhibited rather broad peaks, with few features. Consequently, it was not possible to obtain accurate values of J and d for these complexes. The samples were recrystallized several times and the spectra analyzed by using the total width of the broad patterns, the multiplicity and symmetry given by the crystal structures, and the few resolved peaks as constraints. The tetramethyl- and tetraethylammonium salts, **5** and **6**, respectively, feature cadmium in an octahedral environment, bonded in a facial manner to three nitrogen and three sulfur atoms. In **5**, all nitrogen nuclei are nonequivalent, while in **6** two of the nitrogen nuclei are equivalent (Table 1). The cadmium octahedra are linked via three bridging thiocyanate ligands to form one-dimensional strings of face-sharing octahedra. The higher homologue of **5** and **6**, the tetrapropylammonium salts **12**, has a trigonal bipyramidal coordinated cadmium and was the subject of an earlier solid-state NMR investigation.[19,31b]

The rubidium and cesium salts, **7** and **8**, adopt different structures with two different cadmium sites in each compound. In **7**, one cadmium site is coordinated by two nitrogen atoms in axial positions and four sulfur atoms in equatorial sites, CdN$_2$S$_4$, while the second site is surrounded by two axial sulfur and four equatorial nitrogen atoms, CdN$_4$S$_2$. The octahedra are linked in one direction via corners and in the other direction via edges to form two-dimensional linked planes of octahedra. In accord with this structure, the ^{113}Cd MAS NMR spectrum exhibits two multiplets (Table 1). The high-frequency multiplet is due to the CdN$_2$S$_4$ site (multiplicity similar to **1** and **2**), while the lower frequency multiplet is assigned to the CdN$_4$S$_2$ site. The CdN$_4$S$_2$ site contains two types of nitrogens.

The cesium salt, **8**, adopts an interesting structure in which one cadmium is coordinated by six sulfur atoms, while a second cadmium is surrounded by six nitrogen atoms. The octahedra are linked via the corners in all directions to form a three-dimensional network. The ^{113}Cd MAS NMR spectrum is in agreement with this structure. At high frequency, a single peak of 80-Hz line width, attributed to the CdS$_6$ site, was observed while at relatively low frequency a broad peak of 480-Hz line width due to the CdN$_6$ site was observed. Since the six nitrogen nuclei of the CdN$_6$ site constitute three pairs of nonequivalent nuclei and the peak is featureless, we were unable to analyze this pattern fully. Note that the ^{113}Cd MAS NMR spectrum will consist of 3^6 = 729 transitions for this site! The relatively large line width of the CdS$_6$ site, 80 Hz, probably arises from long-range coupling to six nitrogens.

It is interesting to note that in the case of complex **7** or **8** it would be difficult or impossible to deduce the presence of two distinct cadmium sites using vibration spectroscopy. Only *N,S*-bridging ligands would be identified using this technique.

1:4 Complexes. In compounds **9–11**, the cadmium to thiocyanate molar ratio is 1:4. The bis(tetramethylammonium) salt (NMe$_4$)$_2$[Cd(SCN)$_4$], **9**, forms chains of corner-sharing octahedra. Cadmium is coordinated by four nitrogen atoms and two sulfur atoms. While the two axial bonded thiocyanate moieties are terminal and *N*-bonded, the four SCN ligands in the equatorial plane are bridging with the two sulfur atoms arranged trans to each other. A crystallographic C_2 axis results in two pairs of nitrogen nuclei, the Cd,N bond distances differ by 0.1 Å. The results from an analysis of the complex multiplet in the ^{113}Cd CP/MAS NMR spectrum (Table 1), shown in Figure 5, are in agreement with this structure. Hence, two ^{14}N nuclei result in

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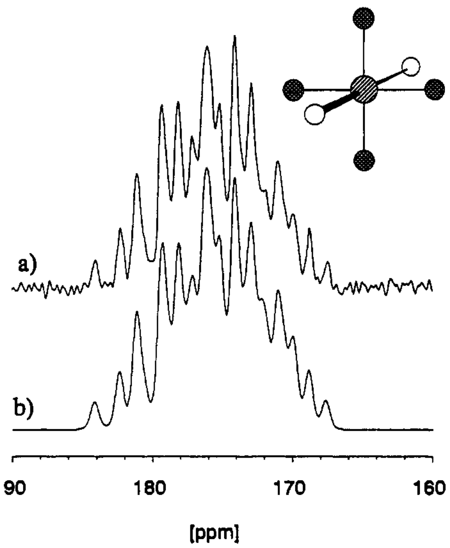

Figure 5. Isotropic region of the ^{113}Cd CP/MAS NMR spectrum of $(Me_4N)_2[Cd(SCN)_4]$, **9**, showing spin–spin coupling of ^{113}Cd with four ^{14}N nuclei: (a) experimental spectrum obtained at a spinning rate of 3345 Hz, recycle delay 8 s, contact time 12 ms, 6590 scans; (b) calculated spectrum.

strong coupling, 117 Hz, while the coupling to the two other ^{14}N nuclei is much smaller, 66 Hz.

In the ^{113}Cd CP/MAS NMR spectrum of the dipotassium salt $K_2[Cd(SCN)_4]\cdot 2H_2O$, **10**, a multiplet similar to the one observed for $Cd(SCN)_2\cdot NH_3$, **2**, is apparent. Thus, the multiplicity indicates that cadmium is directly bonded to two equivalent nitrogen nuclei. This agrees with the results of X-ray diffraction experiments which indicate that the nitrogen atoms occupy the axial positions of the octahedral environment, CdN_2S_4.[43] The Cd–N distances are rather long (Table 1) and the values of J and d are relatively small. However, the chemical shift anisotropy of this compound is clearly the largest of all the octahedral complexes studied here, $\delta_{11} = 395$, $\delta_{22} = 274$, and $\delta_{33} = 206$ ppm, as determined from the ^{113}Cd NMR line shape of a static sample.

The ^{113}Cd CP/MAS NMR spectrum of the mixed cyanide/thiocyanate complex $K_2[Cd(CN)_2(SCN)_2]\cdot 4H_2O$, **11** (Figure 1), has already been discussed. After a period of 2 months, the ^{113}Cd CP/MAS spectrum of **11** had changed exhibiting only a single peak at 569.6 ppm. This peak is assigned to the tetrahedral $Cd(CN)_4^{2-}$ species which we have studied in a pure solid sample of $K_2Cd(CN)_4$.[44] Apparently, the ^{113}Cd NMR peaks due to a species $K_2Cd(SCN)_4\cdot xH_2O$ are sufficiently weak and/or broad to escape detection. It is clear that the octahedral species, CdN_2S_4, observed in compound **10** was not present. Repeated attempts to prepare the sample of stoichiometry $K_2[Cd(CN)_2(SCN)_2]\cdot 4H_2O$ which gave a ^{113}Cd CP/MAS spectrum analogous to that shown in Figure 1 have failed. Clearly, further investigations are necessary in order to establish the products obtained from the reaction of $Cd(SCN)_2$ with KCN. We decided to present the spectrum shown in Figure 1 since it represents the simplest type of ^{113}Cd NMR spectrum showing the effect of spin–spin interactions between ^{113}Cd and ^{14}N.

Structures of Cadmium Thiocyanate Complexes. In solution, X-ray diffraction and Raman experiments have established that cadmium thiocyanate complexes exist as mixtures of tetrahedral and octahedral species involving both the thiocyanate ligand and solvent molecules. The predominant coordination mode of the SCN^- moiety depends on the solvent.[45] Although the ratio cadmium:thiocyanate varies from 1:2 to 1:4 in the compounds studied here, octahedral coordination with the thiocyanate ligand is clearly preferred in the solid state. The only exception so far is $(N\text{-}n\text{-}Pr_4)[Cd(SCN)_3]$, **12**, which has a trigonal bipyramidal configuration[23] and the ^{113}Cd and ^{13}C CP/MAS NMR spectra of which have been discussed in previous communications.[19,31b] Even though a variety of structures were adopted by the cadmium complexes **1**–**10**, in no case was the formation of alternative packings evident from the ^{113}Cd MAS NMR spectra. Obviously, the cadmium thiocyanate system is a class of compounds which is very finely tuneable by subtle variations in stoichiometry and counterion. Although ^{113}Cd NMR studies of some solid cadmium cyano complexes indicate static disorder of the cyanide ion,[34,46] no evidence for disorder of the thiocyanate ion was found in compounds **1**–**10**. In summary, the coordination of cadmium deduced from the ^{113}Cd MAS NMR spectra is in excellent agreement with the reported crystal structures, where applicable.

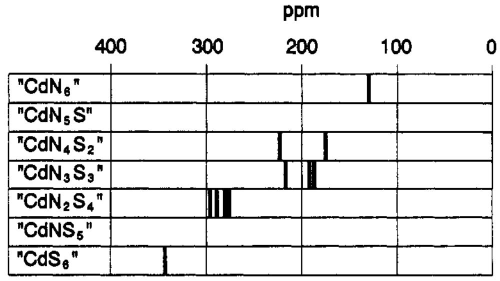

Figure 6. Dependence of the isotropic ^{113}Cd chemical shift on the coordination mode of the thiocyanate ligands, where S and N indicate the thiocyanato and isothiocyanato coordination mode of SCN in octahedral complexes.

Relationship between ^{113}Cd Chemical Shifts and the Number of S-Bonded Thiocyanate Ligands. The dependence of the ^{113}Cd chemical shift on the coordination sphere, CdN_nS_{6-n}, of cadmium is illustrated in Figure 6. Included are only compounds in which cadmium is coordinated by six thiocyanate ligands. Even though the graph has gaps, with examples for the CdN_5S and $CdNS_5$ missing, the trend is clear. Replacement of an *N*-bonded thiocyanate ligand by an *S*-bonded thiocyanate ligand causes an average shift of 38 ppm to higher frequency. The deshielding caused by an increasing number of S atoms is in agreement with the order of shielding contributions of ligands to cadmium chemical shifts established by Ellis *et al.* in an extensive set of single-crystal ^{113}Cd NMR experiments and other solid-state ^{113}Cd NMR investigations, *i.e.*, S > N > O.[47] Similar deshielding effects of the *S*-bonded thiocyanate ligand on transition metal shielding were observed for ^{93}Nb in solution,[11] while ^{103}Rh shows the reversed order, *i.e.*, on average an increase in shielding of 540 ppm per replacement of N by S.[12]

Qualitatively, the trends are rationalized as follows.[47,48] As Cd^{2+} is a d^{10} metal, the filled d subshells make no contributions to the paramagnetic shielding term; the free Cd^{2+} is the species of highest shielding. Deshielding due to paramagnetic contributions is caused by donation of electrons from ligands to the outer p-orbitals of the metal (p-mechanism) and by back-donation of electrons from metal d-orbitals to the ligands, creating "holes"

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in the valence d-orbitals of the metal (d-mechanism). For ^{113}Cd, the p-mechanism is thought to be more important than the d-mechanism,[48a] hence, the ^{113}Cd chemical shift reflects the ability of the ligand to donate electrons into the p-orbitals of the cadmium. It should be noted that for other species in which cadmium is surrounded by six nitrogen donor ligands, ^{113}Cd chemical shifts on the order of 230–380 ppm have been reported,[17b,e] while in the present study the CdN_6 species (Figure 6) has a chemical shift of 130 ppm. It appears that the nitrogen in the thiocyanate ligand is a much harder base than typical nitrogen donor ligands, in agreement with Pearson's concept of hard and soft acids and bases.[16] Unfortunately, the donor properties of the sulfur atom in the thiocyanate cannot be compared with other sulfur donor ligands since there are no reliable chemical shift data for cadmium surrounded by six sulfur donor ligands; they generally form tetrahedral species, with trigonal bipyramidal being the exception.[17b,e]

It is evident that the ^{113}Cd chemical shift may serve as an approximate indication for the value of *n* in the determination of the coordination sphere of solid cadmium complexes, CdN_nS_{6-n}. In addition to the ligand type, the coordination number of the cadmium influences the chemical shift as well.[49] The compound $(N\text{-}n\text{-}Pr_4)[Cd(SCN)_3]$, **12**, with cadmium in a trigonal bipyramidal structure has a chemical shift of 310 ppm,[19] which is at the high-frequency end of the chemical shift range of octahedral thiocyanate complexes found here (Figure 6) and is in agreement with the shielding pattern observed for cadmium, *i.e.*, tetracoordinated < pentacoordinated < hexacoordinated.[17b,e] Also, the chemical shift tensor of this compound displays a significantly larger anisotropy, $\Delta\delta = \delta_{11} - \delta_{33} = 340$ ppm, while $\Delta\delta$ of the octahedral complexes is usually significantly smaller than 200 ppm; hence, with few exceptions, no efforts were made to extract this parameter from the ^{113}Cd NMR spectra.

Relationship between $J(^{113}Cd,^{14}N)$ and r_{CdN}. More reliable information concerning the coordination of cadmium in these compounds originates from the multiplicity observed in the ^{113}Cd NMR spectra. The multiplicity gives the number of ^{14}N nuclei directly bonded to cadmium. Furthermore, the magnitudes of the indirect spin–spin coupling constants obtained in the present study vary over a wide range, *i.e.*, 37–178 Hz; the smallest and largest values of *J* differ by 140 Hz! In line with this observation is the fact that the Cd–N distances vary widely for those compounds for which crystal structures are available. For example, the shortest Cd–N separation occurs in $(N\text{-}n\text{-}Pr_4)[Cd(SCN)_3]$ (2.163 Å), while the largest Cd–N distance can be found in **10**, with $r_{CdN} = 2.45$ Å. In Figure 7, the observed values of *J* versus the Cd–N separations are plotted. For compounds where several nonequivalent ^{14}N nuclei were present, we assigned the nuclei to specific Cd–N distances following the empirical rule proposed here. However, there are sufficient unambiguous systems to support our conclusions, and even with the alternative assignments the overall trend is obvious. The interpretation of the different magnitudes of $^1J(^{113}Cd,^{14}N)$ as arising from variations in r_{CdN} is simplified, since the environment of cadmium is different for the various compounds investigated here and this may account for the scattering of the individual data points. Included in Figure 7 are the values for $Cd(SCN)_2P(3\text{-}CH_3C_6H_4)_3$, 89 Hz (2.256 Å) and 63 Hz (2.297 Å).[50,51] Similar trends were reported for $^1J(M,^{31}P)$ in transition metal phosphine complexes, where M = ^{195}Pt,[52–55] ^{107,109}Ag,[56] and ^{63,65}Cu.[57] Since the indirect spin–spin coupling constant depends on several contributions,[37] there exists no clear and simple analytical relationship to describe the dependence of ^1J on the distance observed in experiments as shown in Figure 7 and elsewhere.[52–55]

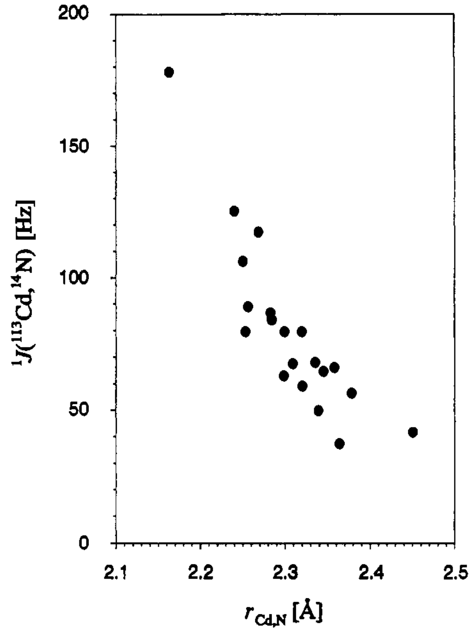

Figure 7. Dependence of $^1J(^{113}Cd,^{14}N)$ on the Cd-N distance. Experimental points are represented by solid circles.

Variations in *d*. The values of *d* reported in Table 1 are small and relatively constant; 18 of the 22 values reported fall in the range 3.5–5.0 Hz. Recall that *d* is proportional to the product $D\chi f(\alpha^D,\beta^D,\eta)$, where $f(\alpha^D,\beta^D,\eta)$ depends on the orientation of the ^{14}N EFG tensor relative to the ^{113}Cd,^{14}N dipolar vector. In the series of compounds investigated, the ^{113}Cd,^{14}N direct dipolar coupling constant, *D*, varies between −191 Hz ($r_{CdN} = 2.163$ Å) and −131 Hz ($r_{CdN} = 2.45$ Å), a decrease of 30% with increasing bond length. On the other hand, the ^{14}N nuclear quadrupolar coupling constant, χ, is expected to increase with longer Cd–N distances. For example, for the shortest Cd–N bond distance in $(N\text{-}n\text{-}Pr_4)[Cd(SCN)_3]$, χ was estimated to be −0.9 MHz, while the longer bonds resulted in values of −1.9 and −2.0 MHz. NQR experiments indicated values in the range 0.4–1.5 MHz for thiocyanate *N*-coordinated to a variety of metals, 2.4–2.6 MHz in KSCN and LiSCN, and 2.9–3.5 MHz in *S*-coordinated thiocyanate compounds.[38] Often, the longer Cd–N distances are related to smaller Cd–N–C angles, ranging from 116 to 170° in the compounds studied here. This will affect the angle β^D and η and reduce the value of *d*. All these facts together may explain the rather small variations in *d*. Further information could be obtained if reliable ^{14}N NQR data were available. For example, the present data allow no conclusions about the presence or absence of anisotropy in the ^{113}Cd,^{14}N indirect spin–spin coupling.

Conclusions

The present study demonstrates the power of ^{113}Cd MAS NMR in characterizing cadmium thiocyanate coordination complexes in the solid state. The multiplicity due to ^{113}Cd,^{14}N spin–spin coupling observed in this study is unprecedented in the solid-state

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NMR literature. Analysis of this multiplicity yields the number of nitrogen atoms directly attached to cadmium. Moreover, the magnitude of $^1J(^{113}\text{Cd},^{14}\text{N})$ provides an estimate of the cadmium–nitrogen separation. Characterization of the cadmium chemical shift tensor can provide information concerning the coordination number of cadmium and the number of directly attached sulfur ligands. Clearly, the results of this study establish benchmarks for future studies of cadmium thiocyanates, cyanates, and selenocyanates. NQR studies on some of these complexes would be of great interest in order to allow for a detailed analysis of the residual dipolar coupling, d, and to assess the possibility of anisotropy in the $^{113}\text{Cd},^{14}\text{N}$ indirect spin–spin coupling tensor.

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