

The Cyanurate Ribbon in Structural Coordination Chemistry: An Aggregate Structure That Persists across Different Coordination Environments and Structural Types

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Abstract: A series of nine coordination compounds is described, in which a common supramolecular structure, a ribbon of cyanurates, persists across variations in the metal center, coordination geometry, coordination environment, and crystal type. The syntheses and solid-state structures, as determined by single-crystal X-ray diffraction, are described for six of the complexes, *trans*-[Cu(cyan- κ N)₂(H₂O)₂] \cdot 2Na(cyan) \cdot 4H₂O (**1**), *trans*-[Cu(cyan- κ N)₂(NH₃)₂] (**5**), *trans*-[Cu(cyan- κ N)₂(NH₃)₂]*trans*-[Cu(cyan- κ O²)₂(NH₃)₄] (**6**), *trans*-[Ni(cyan- κ N)₂(NH₃)₄] (**7**), (OC-6-33)-[Ni(cyan- κ N)₂(NH₃)₂(H₂O)₂] (**8**), and [Cu(cyan- κ N)(PPh₃)₂] \cdot 2CDCl₃ (**9**). The results are discussed together with the previously reported structures of the other three complexes, [M(cyan- κ N)(H₂O)₅](cyan) \cdot 2H₂O (M = Mn (**2**), Co (**3**), Ni (**4**)). In all cases, the ribbon of cyanurates is propagated through a recognition interaction involving a pair of hydrogen bonds between adjacent cyanurates, with a topological pattern of the type R₂²(8). In eight of the nine cases, the ribbon is linear, but for compound **5**, which is the first product of the reaction from which compound **6** is derived, the ribbon is crenelled. An unsuccessful attempt to synthesize a product without the cyanurate ribbon in the solid state is described. The possibility that the cyanurate ribbon represents a traditional self-assembly in some of these systems but not in others is discussed. It is concluded that the formation of the cyanurate ribbon is a determinative factor in the solid-state structural coordination chemistry of the cyanurates of metals of the first transition series.

Introduction

During the course of our studies on the coordination chemistry of polyfunctional ligands, we have encountered an aggregate ligand-based supramolecular structure that persists in the solid state across a series of widely varying crystalline environments and which appears to have a significant determinative role in the structural chemistry of these systems.

Polyfunctional ligands, largely organic entities that possess more than one functional group, are capable of bonding to transition metals and at the same time of forming strong interactions with their surroundings in the crystalline state. Thus, complexes of these ligands can be used to prepare solid-state systems in which a transition metal is trapped in a constraining environment that, once formed, limits the ability of the metal to manifest its preferred behavior. The polyfunctional ligands that we have found useful include saccharinate,¹ nicotinate,² and the subject of the present report, isocyanurate.

The use of polyfunctional ligands provides a certain degree of coarse tuning of the stress caused at transition-metal centers, since the ligands can be chosen from an abundant selection of sizes and shapes, with additional choice over the number, nature, and disposition of the functional groups on the ligand, and thus with some control over the disposition of hydrogen-bond donors and acceptors.³

We recently reviewed the coordination chemistry of isocyanurate, the tri-keto tautomer, which is the form found in all of

the complexes in the present study.⁴ Briefly, cyanurates of copper were prepared as long ago as 1847.⁵ Later in the 19th century, cyanurates were reported for magnesium, manganese, cobalt, nickel, and zinc.⁶ Many of the same compounds were prepared more recently, from melts,⁷ and a crystal structure determination using photographic techniques was reported for the complex *trans*-[Cu(cyan- κ N)₂(NH₃)₂].⁸ Preparations and noncrystallographic characterization have been reported for cyanurates of nine other metals by Seifer and co-workers.⁹ The preparations reported in the late 19th century have also been repeated within the last decade or so,¹⁰ and a crystal structure was reported for a cobalt compound with overall stoichiometry

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(7) Taylor, R. M. *Z. Anorg. Allg. Chem.* **1972**, 390, 85–96.

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Table 1. Selected Bond Distances (Å) and Angles (deg) from the Crystal Structures of **1** and **5–9**

	distances		angles
(a) [Cu(cyan-κN) ₂ (H ₂ O) ₂] ₂ ·2Na(cyan)·4H ₂ O (1)			
Cu(1)–O(1)	1.929(3)	O(1)–Cu(1)–N(1)	89.71(10)
Cu(1)–N(1)	1.949(2)		
(b) <i>trans</i> -[Cu(cyan-κN) ₂ (NH ₃) ₂] (5)			
Cu(1)–N(6)	1.994(3)	N(6)–Cu(1)–N(1)	90.56(11)
Cu(1)–N(1)	2.099(2)		
(c) <i>trans</i> -[Cu(cyan-κN) ₂ (NH ₃) ₂] <i>trans</i> -[Cu(cyan-κO) ₂ (NH ₃) ₄] (6)			
Cu(1)–N(1)	2.000(7)	N(1)–Cu(1)–N(13)	90.3(3)
Cu(1)–N(13)	2.023(8)	N(14)–Cu(2)–N(15)	91.8(3)
Cu(2)–N(14)	1.998(7)	N(14)–Cu(2)–O(10)	90.9(3)
Cu(2)–N(15)	2.014(8)	N(15)–Cu(2)–O(10)	89.9(3)
Cu(2)–O(10)	2.602(6)		
(d) <i>trans</i> -[Ni(cyan-κN) ₂ (NH ₃) ₄] (7)			
Ni(1)–N(5)	2.069(3)	N(5)–Ni(1)–N(4)	91.81(11)
Ni(1)–N(4)	2.073(3)	N(5)–Ni(1)–N(1)	90.46(4)
Ni(1)–N(1)	2.285(2)	N(4)–Ni(1)–N(1)	89.53(4)
		N(4)–Ni(1)–N(4 ^a)	87.2(2)
		N(5)–Ni(1)–N(5 ^a)	89.2(2)
		N(5)–Ni(1)–N(4 ^a)	179.02(12)
		N(1)–Ni(1)–N(1 ^b)	178.70(12)
(e) (OC-6-33)-[Ni(cyan-κN) ₂ (NH ₃) ₂ (H ₂ O) ₂] (8)			
Ni(1)–N(2)	2.055(4)	N(2)–Ni(1)–N(4)	94.6(2)
Ni(1)–N(4)	2.053(4)	N(2)–Ni(1)–O(3)	176.0(2)
Ni(1)–O(3)	2.063(3)	N(2)–Ni(1)–O(1)	85.8(2)
Ni(1)–O(1)	2.168(3)	N(2)–Ni(1)–N(1)	91.82(6)
Ni(1)–N(1)	2.247(3)	N(4)–Ni(1)–O(3)	89.4(2)
		N(4)–Ni(1)–O(1)	179.6(2)
		N(4)–Ni(1)–N(1)	92.58(6)
		O(3)–Ni(1)–O(1)	90.22(14)
		O(3)–Ni(1)–N(1)	88.00(6)
		O(1)–Ni(1)–N(1)	87.40(6)
		N(1)–Ni(1)–N(1 ^c)	173.43(12)
(f) [Cu(cyan-κN)(PPh ₃) ₂] (9)			
Cu(1)–N(1)	1.971(5)	N(1)–Cu(1)–P(1)	120.2(2)
Cu(1)–P(1)	2.226(2)	N(1)–Cu(1)–P(2)	110.8(2)
Cu(1)–P(2)	2.241(2)	P(1)–Cu(1)–P(2)	128.94(8)

^a 1 – x, y, 3/2 – z. ^b x, y, 3/2 – z. ^c x, 3/2 – y, z.

[Co(cyan-κN)₂(H₂O)₄]₃·3H₂O.¹¹ We have reported a redetermination of that structure⁴ and have discussed the presence of the cyanurate ribbon in the cobalt and isostructural manganese and nickel systems.

Cyanuric acid has played a role in supramolecular systems outside of coordination chemistry. Whitesides and co-workers have reported extensive studies of complexes of cyanuric acid with melamine.¹² Through the examination of crystalline systems in which cyanuric acid is replaced by its structural quasi-mimetic, 5,5-diethylbarbituric acid, they have also shown that linear and crenelled tapes can be deliberately constructed.¹³ An earlier example of organic crystal engineering involving cyanuric acid gave rise to a crystalline complex of the latter with 8-bromo-9-ethyladenine.¹⁴ Solid-state complexes of cyanuric acid with biuret¹⁵ and with melamine¹⁶ have also been structurally characterized.

In the present study, nine complexes (**1–9** throughout this

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(13) (a) Zerkowski, J. A.; MacDonald, J. C.; Seto, C. T.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 2382–2391. (b) As did the authors of ref 13a, we refer to the tri-keto tautomer of the parent molecule as “cyanuric acid”. We refer to its conjugate base in the tri-keto form as “isocyanurate” or “cyan”, with the suffix “-κN”, for example, used to indicate the ligating atom in a transition-metal complex. We use *cyanurate* as a generic term, indicating for example that a cyanurate ribbon comprises moieties of the same or different origin.

(14) Shieh, H.-S.; Voet, D. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2354–2360.

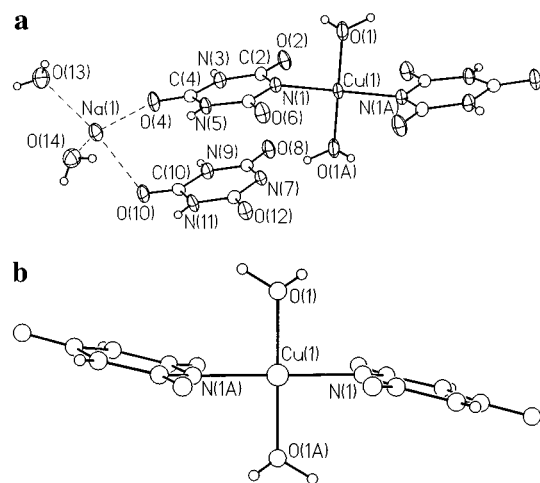


Figure 1. (a) Thermal ellipsoid plot of the contents of one asymmetric unit of the crystal structure of [Cu(cyan-κN)₂(H₂O)₂]₂·2Na(cyan)·4H₂O (**1**), showing the atom naming scheme. Primed atom names signify sites related to their unprimed congeners by an inversion center at Cu(1). Non-hydrogen atoms are represented by their 50% probability ellipsoids. (b) View of the neutral copper complex with the isocyanurate ligands seen side-on.

report) of the polyfunctional ligand isocyanurate (cyan), which crystallize with a broad variety of structural types, are seen to possess a common aggregate structure, an unbounded one-dimensional ribbon of cyanurates. All of the complexes are the products of relatively simple reactions, and the products characterized are, with one exception (**6**), the first and principal products isolated from their respective preparations. In some of the cases, cocrystallization of a neutral isocyanurate-containing complex with a cyanurate salt (**1**), or of cationic isocyanurate-containing complexes with unligated cyanurate (**2–4**) has occurred. In one case (**6**) two different transition-metal complexes—one of them with weakly, unconventionally ligated cyanurates—are found in the solid. In at least the cases in which weakly bound or unligated cyanurate moieties are present along with ligated cyanurate (**1**, **2–4**, and **6**), the overall stoichiometries and the bonding arrangements observed about the transition-metal centers are important for maintaining the integrity of the cyanurate ribbon. The topology of this superstructure is different from those found in the engineered organic systems mentioned above.^{12–14} The linear cyanurate ribbon found in **8** of the 9 structures reported here is similar to that found in crystalline anhydrous cyanuric acid¹⁷ and in potassium cyanurate.¹⁸

Results

trans-[Cu(cyan-κN)₂(H₂O)₂]₂·2Na(cyan)·4H₂O (**1**). Compound **1** crystallizes in the triclinic space group *P* $\bar{1}$ with one formula unit in the unit cell. The bond distances and angles around the copper atom, which lies on a crystallographic inversion center, show no anomalies, as can be seen in Table 1. A thermal ellipsoid plot showing the atom labeling scheme is given in Figure 1a. The isocyanurate ligands, as expected, are bound to the metal through their deprotonated nitrogen atoms.

The extended structure of compound **1** possesses a supramolecular aggregate, namely a ribbon of cyanurates as shown in Figure 2. This cyanurate ribbon is an unbounded, periodic,

(15) Stainton, N. M.; Harris, K. D. M.; Howie, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1781–1784.

(16) Wang, Y.; Wei, B.; Wang, Q. *J. Cryst. Spectrosc. Res.* **1990**, *20*, 79–84.

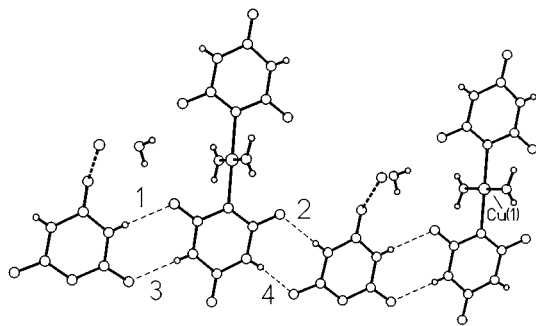


Figure 2. A portion of the cyanurate ribbon from the crystal structure of $[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{H}_2\text{O})_2] \cdot 2\text{Na}(\text{cyan}) \cdot 4\text{H}_2\text{O}$ (**1**). Characteristics of the four unique hydrogen bonds are given in the text and in Table 2.

topologically linear structure formed by both the copper-bound and unligated cyanurates. Each link in the cyanurate ribbon is held to the next by a pair of hydrogen bonds with donor-acceptor distances of about 2.8 Å (Table 2), formed by self-complementary (H)N–C(=O) groups of neighboring bound and unbound cyanurates. Ligated and unligated cyanurate moieties form alternate links of the chain.²⁰

The classification of this ribbon as topologically linear, or one-dimensional, arises from the fact that there is just one propagation operation, namely a 180° rotation about a line that bisects the two *ortho*-C–*meta*-N bonds, combined with translation parallel to the same line. This operation relates adjacent cyanurates along the direction of propagation of the ribbon.

Cyanurate aggregates are ubiquitous in the cyanurate-containing organic systems reported to date. A linear ribbon, practically identical to that in **1**, is observed in the crystal structure of the tri-keto tautomer of cyanuric acid, although the presence of the ribbon was not discussed.¹⁷ Other supramolecular aggregates based on cyanuric acid or on entities related to it, topologically distinct from the present ribbon, have been prepared,^{12–16} as mentioned earlier; and evidence has been presented that indicates that the pattern of mated complementary groups exists in solution.²¹ With regard to the coordination complex **1**, it apparently has never before been synthesized in a laboratory, but its crystal structure has been characterized from a deposit found in a swimming pool.²² The presence of the cyanurate ribbon was not discussed in that report.

A further structural feature of compound **1** worthy of mention is a distortion of the complex by pitching of each of the two cyanurates about an in-plane axis, with the two ligand pitch

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(18) (a) Syssoeva, T. F.; Branzburg, M. Z.; Gurevich, M. Z.; Starikova, Z. A. *Zh. Strukt. Khim.* **1990**, *31*, 90–96; *Chem. Abstr.* **1991**, *114*, 196741g. (b) The presence of the cyanurate ribbon was established by examination of coordinates taken from the Cambridge Structural Database System,¹⁹ reference code VOKKIP.

(19) (a) Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 1. (b) Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 31–37.

(20) (a) The motif formed by this pattern of hydrogen bonding, which gives rise to an eight-membered intermolecular ring, N–H···O=C–N–H···O, can be assigned the topological symbol $R_2^2(8)$, according to the system of Etter, MacDonald, and Bernstein. (b) Etter, M. C.; MacDonald, J. C.; Bernstein, J. *Acta Crystallogr. Sect. B* **1990**, *B46*, 256–262.

(21) Mathias, J. P.; Seto, C. T.; Simanek, E. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 1725–1736.

(22) Hart, R. D.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 1927–1932.

directions concerted in such a way that the complex maintains its center of symmetry (Figure 1b). Such a distortion of a complex by rotation of a ligand away from a symmetrical disposition can be characterized by an angular distortion parameter, which for the purposes of permitting a straightforward discussion of the systems under consideration, will be defined as follows. The angle between the metal–ligand bond–Cu(1)–N(1) in Figure 1—and the external bisector of the angle C(2)–N(1)–C(6), serves as a quantitative indication of the distortion. The traditional term “misdirected valence”, or MDV, could be used for the angular distortion parameter, although in this case the question of misdirected valence turns out to be more involved.²³ For compound **1** the value of the angular distortion parameter is 13.21(7)°.

$[\text{M}(\text{cyan-}\kappa\text{N})(\text{H}_2\text{O})_5](\text{cyan}) \cdot 2\text{H}_2\text{O}$ (M = Mn, **2**; Co, **3**; Ni, **4**). **Selective Crystallization of the Aggregate Structure.** The only aqua-containing complexes of Mn, Co, and Ni with cyanurate are those previously described as long as a century ago⁶ and accurately characterized more recently.^{4,10,11} Although their stoichiometry corresponds to a formulation containing what would be the predicted neutral complex, $[\text{M}(\text{cyan-}\kappa\text{N})_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$, it turns out that the transition-metal complex in each case is cationic, with five aqua ligands and a single metal-bound isocyanurate. As described in our previous report on these three complexes,⁴ both the ligated and “free” isocyanurates participate in the formation of a cyanurate ribbon, almost identical in its shape to that observed in compound **1** (Table 2). In all three structures, the fifth aqua ligand, that *trans* to isocyanurate in the complex, takes part in hydrogen bonding that cross-links the cyanurate ribbons (Figure 3). The metal–ligand bond distances in the three complexes follow faithfully the expected trends on passing from manganese to cobalt to nickel.²⁴ The only unpredicted feature in each case is the crystallization of a cationic pentaqua, monoisocyanurato complex, with an unligated isocyanurate present in the crystallographic asymmetric unit, instead of the neutral bis-isocyanurato complex.

trans- $[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{NH}_3)_2]$ (**5**) and *trans*- $[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{NH}_3)_2] \text{trans-}[\text{Cu}(\text{cyan-}\kappa\text{O})_2(\text{NH}_3)_4]$ (**6**). **Structural Isomerism of the Cyanurate Ribbon.** Compound **5** was reported by Taylor⁷ and by Slade, Raupach, and Radoslovich,⁸ who prepared the complex from the metal halide in molten urea. We synthesized the complex using solution methods and repeated the structure determination. The copper center has distorted square-planar coordination, and the bond distances and angles around the metal are, once again, within the ranges expected for this type of complex (Table 1b). A drawing of the complex is given in Figure 4. There is essentially no element of misdirected valence in this complex; the angular distortion parameter (*vide supra*) has a value of 4.4°. Unlike the aqua-containing systems **1–4**, the transition-metal complex is the only entity present in the crystal structure of **5**. The cyanurate ribbon in **5** is an isomer of that seen in the other compounds; in the others the ribbon is based on side-on contacts of adjacent isocyanurates disposed in such a way that the *ortho*-carbonyl of one isocyanurate acts as an acceptor for a hydrogen bond from the *meta*-(NH) moiety of the second, and *vice versa* (Figure 2). In compound **5**, however, the intermolecular interactions are organized in such a way that the cyanurate ribbon is crenelled. With reference to Figure 5, we see that there is one contact consisting of a pair of hydrogen bonds based

(23) The possibility of rehybridization of the deprotonated nitrogen of the nonaromatic tri-keto tautomer of cyanurate raises the question of whether there is misdirected valence or whether partial rehybridization permits the cyanurate to maintain a full σ -bond to the metal.

(24) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Quesada, J. F. *Inorg. Chem.* **1993**, *32*, 4861–4867.

Table 2. Geometrical Parameters for the Cyanurate Ribbons in Complexes 1–9

complex	D—H...A	D...A (Å)	H...A (Å)	D—H...A (deg)	acceptor coordinates	ref
1	N(9)—H(9)...O(2) ^b	2.813(3)	2.10(3)	172(3)	1 - x, 1 - y, 1 - z	this work
	N(11)—H(11)...O(6) ^c	2.834(3)	2.10(3)	175(3)	-x, -y, 2 - z	
	N(5)—H(5)...O(12) ^d	2.798(3)	2.06(3)	171(3)	-x, -y, 2 - z	
	N(3)—H(3)...O(8) ^e	2.788(3)	2.10(3)	170(3)	1 - x, 1 - y, 1 - z	
2	N(13)—H(13)...O(26)	2.801(3)	1.92(3)	170(2)	x + 1, y, z	a
	N(15)—H(15)...O(6)	2.955(3)	2.04(3)	173(2)	x + 1/2, 1/2 - y, z - 1/2	
	N(23)—H(23)...O(16)	2.919(3)	2.02(3)	172(2)	x + 1/2, 1/2 - y, z - 1/2	
	N(25)—H(25)...O(12)	2.834(3)	1.96(3)	168(2)	x - 1, y, z	
3	N(13)—H(13)...O(26)	2.780(5)	1.79(5)	156(4)	x + 1, y, z	a
	N(15)—H(15)...O(6)	2.876(5)	1.96(5)	171(4)	x + 1/2, 1/2 - y, z - 1/2	
	N(23)—H(23)...O(16)	2.823(5)	1.96(5)	173(4)	x + 1/2, 1/2 - y, z - 1/2	
	N(25)—H(25)...O(12)	2.825(5)	1.96(4)	165(4)	x - 1, y, z	
4	N(13)—H(13)...O(26)	2.791(7)	1.80(8)	162(7)	x + 1, y, z	a
	N(15)—H(15)...O(6)	2.859(7)	1.97(8)	170(7)	x + 1/2, 1/2 - y, z - 1/2	
	N(23)—H(23)...O(16)	2.816(7)	2.11(5)	156(8)	x + 1/2, 1/2 - y, z - 1/2	
	N(25)—H(25)...O(12)	2.829(7)	2.15(5)	161(9)	x - 1, y, z	
5	N(3)—H(3)...O(2) ^f	2.813(3)	1.97(4)	177(3)	-x - 1, -y, -z - 1	this work
	N(5)—H(5)...O(4) ^g	2.813(3)	1.93(4)	173(3)	1 - x, 1 - y, 1 - z	
6 ^h	N(5)...O(8) ⁱ	2.769(10)			x, y, z - 1	this work
	N(7)...O(6) ^j	2.819(9)			x, y, z + 1	
	N(11)...O(2) ^k	2.779(10)			x, y, z	
	N(3)...O(10) ^l	2.813(9)			x, y, z	
7	N(3)—H(3)...O(2)	2.891(2)	1.99(3)	176(2)	1/2 - x, 1/2 - y, 1 - z	this work
8	N(5)—H(5)...O(6)	2.837(3)	1.98(5)	175(7)	-x - 1, 1 - y, -z	this work
	N(3)—H(3)...O(2)	2.819(3)	2.00(5)	169(3)	1 - x, 1 - y, 1 - z	
9	N(2)—H(2)...O(1) ^m	2.805(8)	1.95(1)	175(6)	1 - x, -y, 1 - z	this work
	N(3)—H(3)...O(3) ⁿ	2.791(8)	1.96(2)	165(6)	2 - x, -y, 1 - z	

^a Reference 4. ^b Hydrogen bond labeled "1" in Figure 2. ^c Labeled "2" in Figure 2. ^d Labeled "3" in Figure 2. ^e Labeled "4" in Figure 2. ^f Labeled "1" in Figure 5. ^g Labeled "2" in Figure 5. ^h Hydrogen atoms were omitted from the structural model for compound 6. ^{i-l} Labeled "1", "2", "3", and "4", respectively, in Figure 7. ^m Labeled "1" in Figure 12. ⁿ Labeled "2" in Figure 12.

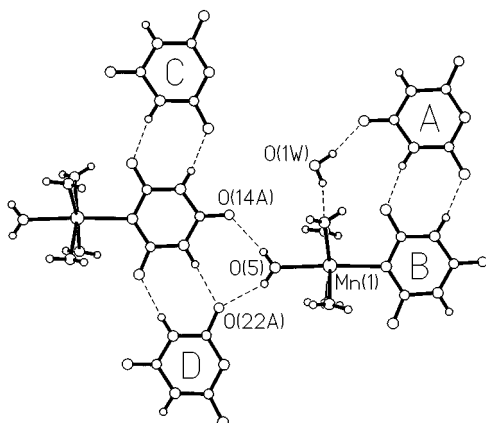


Figure 3. Sections of two adjacent cyanurate ribbons, one involving rings labeled A and B, the other C and D, from the crystal structure of [Mn(cyan-κN)(H₂O)₅](cyan)·2H₂O (**2**). The fifth aqua ligand, O(5), forms H-bonds with the adjacent ribbon: O(5)...O(14A) = 2.860 (3), O(5)...O(22A) = 2.828 (3) Å. The rings labeled A, C, and D belong to unligated cyanurates.

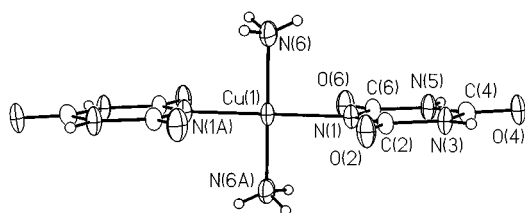


Figure 4. Thermal ellipsoid plot of *trans*-[Cu(cyan-κN)(NH₃)₂] (**5**) from the crystal structure, showing the atom labeling scheme. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

on the *ortho*–*meta* self-complementarity of the isocyanurate ligand, as in the other cases. But then the next link in the chain consists of a pair of hydrogen bonds between complementary *meta*–(NH) and *para*–(C=O) groups of neighboring isocyanurates, giving the bends in the chain. Each link in the chain still

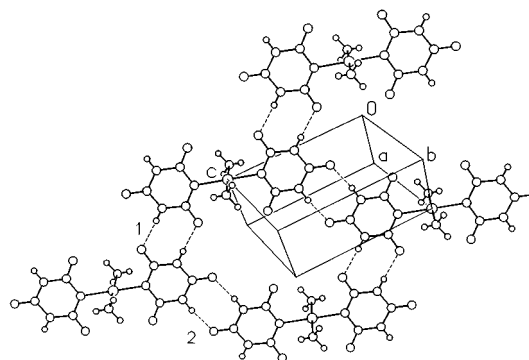


Figure 5. The topologically crenelled cyanurate ribbon, from the crystal structure of **5**.

has an eight-membered ring topology $R_2^2(8)$.^{20b} Considering only the topological properties of the crenelled ribbon, there is still a single propagation vector, which in this case relates a basic unit consisting of two cyanurates to the next such unit along the chain.

The disposition of the cyanurate ribbon in compound **5** naturally led to the question of whether this is the only possibility for this particular chemical system. We found that further treatment of the reaction mixture from which compound **5** had been isolated leads to the formation of a second stable compound, **6**, which can be isolated as a pure, twinned crystalline sample.

Compound **6**, *trans*-[Cu(cyan-κN)₂(NH₃)₂]*trans*-[Cu(cyan-κO²)₂(NH₃)₄], is obtained by successive recrystallization of **5** from an aqueous solution containing concentrated ammonium hydroxide. After this treatment, no further yield of **5** is obtained. As we were unable to isolate single crystals of **6**, we proceeded with the structure determination using a double crystal and took steps to separate the diffraction patterns. The procedure used is described in the Supporting Information. One formula, shown in Figure 6, comprises one unit of *trans*-[Cu(cyan-κN)₂(NH₃)₂],

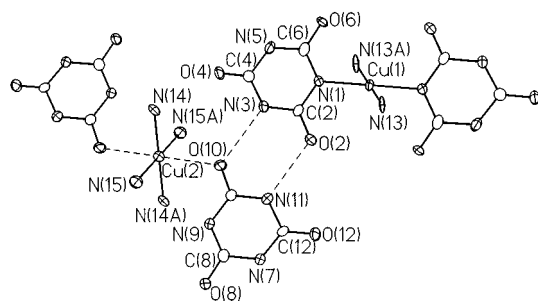


Figure 6. One formula unit of *trans*-[Cu(cyan- κ N)₂(NH₃)₂]*trans*-[Cu(cyan- κ O)₂(NH₃)₄] (**6**) from the crystal structure. The copper atoms lie on crystallographic inversion centers.

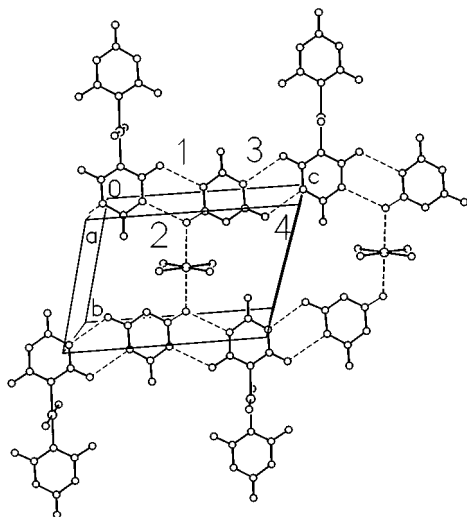


Figure 7. The extended solid-state structure of **6**, showing the linear cyanurate ribbon and the interstitial nature of the [Cu(NH₃)₄]²⁺ units.

the same moiety found in compound **5**, plus one unit of [Cu(NH₃)₄]²⁺, and two cyanurate ions. Both copper atoms lie on centers of symmetry, and the covalent bond distances about them are typical of Cu(II) (Table 1c). Each of the two "loose" cyanurate ions makes a contact of 2.602(6) Å with Cu(2), the central copper atom of [Cu(NH₃)₄]²⁺—close enough to be called a bond—so that the complex could also be described as *trans*-[Cu(cyan- κ O)₂(NH₃)₄]. This contact with copper involves the *ortho*-carbonyl oxygen atom of the cyanurate, and not the charge-bearing deprotonated nitrogen, which has no covalent contact. That the nitrogen still is the charge-bearing entity is seen in the bond distances in the cyanurate, which indicate that no change of tautomer has occurred.

The most noteworthy feature of the structure of **6** is that the cyanurate ribbon has returned to its normal linear topology. As seen in Figure 7, the bound and "loose" isocyanurate moieties form alternate links in the cyanurate ribbon, which is identical in shape (Table 2) to the ribbons found in compounds **1**–**4**. The aggregate is once again extended by a double hydrogen-bonding interaction between complementary *ortho*-(C=O)–*meta*-(NH) pairs from adjacent isocyanurate moieties.

***trans*-[Ni(cyan- κ N)₂(NH₃)₄] (**7**) and (*OC*-6-33)-[Ni(cyan- κ N)₂(NH₃)₂(H₂O)₂] (**8**).** Compound **7** can be synthesized by the reaction of a nickel halide with cyanuric acid in a hot concentrated aqueous solution of ammonium hydroxide. The complex is six-coordinate and has bond distances and angles typical of such a system (Table 1d). The coordination octahedron consists of a square plane of ammine ligands about the central nickel, with N-ligated isocyanurate more weakly bonded at the fifth and sixth sites (Figure 8). The isocyanurate ligands are pitched out of the central molecular plane, with both ligands

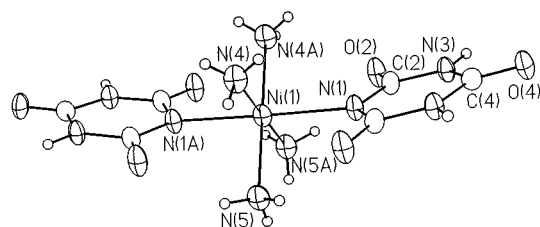


Figure 8. Thermal ellipsoid plot of one molecule of *trans*-[Ni(cyan- κ N)₂(NH₃)₄] (**7**), showing the atom labeling scheme. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

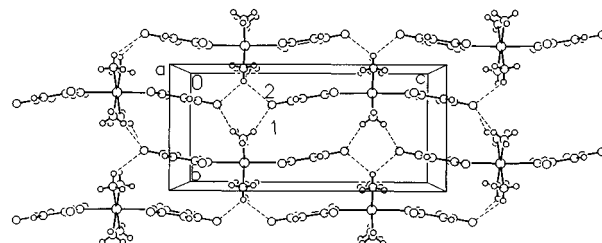


Figure 9. Extended structure of **7** in the solid state. The cyanurate ribbons are extended in the direction perpendicular to the plane of the figure. The hydrogen bond labeled "1" has an N···O distance of 3.069(3) Å, and the N···O distance for the interaction labelled "2" is 3.138(3) Å.

displaced in the same direction, so that the overall molecular symmetry is *C*_{2v}. The molecules are packed in the crystal in such a way that isocyanurate ligands from adjacent molecules form a cyanurate ribbon, which is propagated in the direction parallel to the crystallographic *x* axis, and which is held together by hydrogen bonds with parameters very similar to those found for all of the other ribbons (Table 2). The cyanurate ribbons are stacked parallel to the crystallographic *y* axis, as shown in Figure 9, with a stacking distance of about 3.5 Å. The angular distortion parameter has a value of 8.2°.

It is possible to exchange two of the ammine ligands of compound **7** for water, through prolonged boiling of **7** in an aqueous solution containing NH₄OH, giving [Ni(cyan- κ N)₂(NH₃)₂(H₂O)₂] (**8**) in which the cyanurate ligands are still *trans* to each other, but which has the two aqua ligands in a relative *cis* disposition. The identity of each of the small ligands was clear from the X-ray structure, in which all of the hydrogen atoms were located and refined independently (with a common isotropic displacement parameter) without problems. The stoichiometry thus determined accords with the elemental analysis and IR spectral data. The solid-state structure of **8** is a monoclinic distortion of the structure of **7**,²⁵ with the nickel atom and the four small ligands residing on a crystallographic mirror plane in space group *P*2₁/*m*. Once again the cyanurate ribbon is present, with geometrical parameters as given in Table 2. A drawing of the molecule is shown in Figure 10, and the bond distances around the central nickel atom are given in Table 1e. The pitching of the cyanurate ligands away from a symmetrical disposition is far more pronounced in the bis-aqua complex **8**, giving a dihedral angle of 31.6° between the planes of the two rings, and an angular distortion parameter of 11.5°.

(25) The relationship between the two structures can be seen by applying the following transformation to the unit cell of **8**:

$$\begin{bmatrix} a' \\ b' \\ c' \end{bmatrix} \begin{bmatrix} 1 & 0 & -1 \\ 1 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

The resulting C-centered cell has $a' = 11.211$, $b' = 7.281$, $c' = 16.022$ Å; $\alpha' = 90$, $\beta' = 90$, $\gamma' = 96.44^\circ$; and $V = 1299.8$ Å³. That this is a distortion of the structure of **7** can be seen by comparison of the unit cell of the latter (Table 3) with these values.

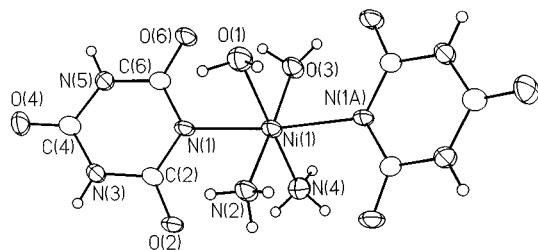


Figure 10. Thermal ellipsoid plot of one molecule of (OC-6-33)-[Ni(cyan- κ N)₂(NH₃)₂(H₂O)₂] (**8**) from the crystal structure. Non-hydrogen atoms are represented by their 50% probability ellipsoids.

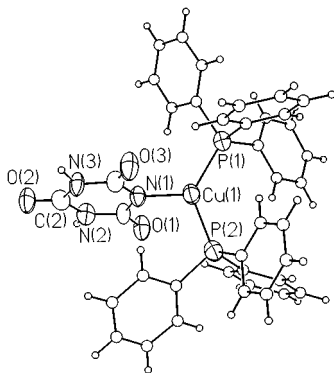


Figure 11. Thermal ellipsoid plot of [Cu(cyan- κ N)(PPh₃)₂] (**9**), showing the atom naming scheme for the coordination shell. Non-hydrogen atoms are represented by their 50% probability ellipsoids, except for the phenyl carbon atoms, which are shown as circles of arbitrary radius.

An Attempt To Break the Cyanurate Ribbon: [Cu(cyan- κ N)(PPh₃)₂] \cdot 2CDCl₃, (**9**). In order to assess the level of persistence possessed by the cyanurate ribbon in transition-metal complexes, we prepared [Cu(cyan- κ N)(PPh₃)₂] (**9**) a complex of Cu(I) with two bulky hydrophobic ligands. This was expected to yield a solid-state environment unfavorable to the pairwise formation of hydrogen bonds necessary for the existence of the cyanurate ribbon. As it turned out, the ribbon was still present.

A drawing of one molecule of compound **9** is given in Figure 11, and the bond distances and angles around the copper center are collected in Table 1f. The copper atom is three-coordinate, and essentially planar. The cyanurate ligand makes a dihedral angle of 75.2(1) $^\circ$ with the plane of the three coordinated atoms. The two triphenylphosphine ligands are splayed away from each other, giving a value of 128.94(8) $^\circ$ for the angle P(1)–Cu(1)–P(2). Although a view of just the molecule implies an imposing domination of its surface by the six phenyl groups, in the solid this complex still manages to pack in such a way as to permit the formation of the cyanurate ribbon. The hydrogen-bonding parameters of the aggregate structure, collected in Table 2, are quite similar to those of all of the other systems possessing the linear ribbon. The packing in the solid comprises a serpentine arrangement of hydrophobic moieties surrounding a channel through which the cyanurate ribbon is threaded, as seen in Figure 12.

Discussion

Persistence and Structural Importance of the Cyanurate Ribbon. The most commanding feature of the results reported here is the persistence of the cyanurate ribbon in the solid state across a series of complexes with different metals, different types of coordination shells, different molecular topological environments, and different extended structural types. This unforeseen solid-state structural property of complexes with isocyanurate

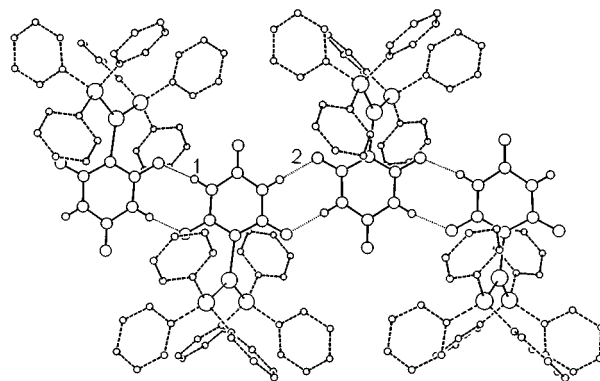


Figure 12. Drawing of part of the extended structure of compound **9**. The cyanurate ribbon runs horizontally through the center of the drawing.

ligands appears not to be just another packing arrangement, but rather to be a determinative entity for structural features all the way down to the level of coordination geometry. Although cyanurate has been used as the basis of designed solid organic systems, the presence in the compounds described here of a transition metal center and other ligands varying in size from water to triphenylphosphine would be expected to impose significant impediments to the formation of a persistent aggregate structure such as the cyanurate ribbon that we observe. Whether the formation of the cyanurate ribbon can be qualified as an overriding consideration in structural coordination chemistry will require more investigation; the present results permit a description of the ribbon as a determinative influence alongside the other factors that enter into play in this chemistry—the coordination preferences of the transition-metal centers, the steric requirements of the other ligands, and the H-bonding capabilities of all of the polar moieties present.

As mentioned earlier, the cyanurate ribbon has a single propagation vector; that is, it is one-dimensional. Considering the linear ribbon as a structural entity in its own right, one can describe its role in the arrangement of each three-dimensional crystal structure much the way that one might do with a discrete molecule. After formation of the ribbon, each cyanurate moiety still has pendant functional groups and polar entities—the charge-bearing nitrogen atom, the *para*-carbonyl group, and the out-of-plane π -clouds of all of the carbonyl groups. The packing of the cyanurate ribbon with the rest of the entities in each crystal thus involves not only ligation to the transition metal center, but also hydrogen bonding to other entities such as ligated and interstitial water in **2–4**, interactions with interstitial metal atoms such as sodium in the structure of **1** or copper in **6**, and stacking with other cyanurate ribbons as is observed in all of the structures with the linear ribbon. While some of the structures have rich three-dimensional patterns of intermolecular interactions, the one-dimensional ribbon of cyanurates is the only supramolecular structure common to all of the systems.

The structure of compound **6** serves as an example of the structural importance of the cyanurate ribbon in these systems. In **6** there is a role reversal between the unligated cyanurate, which would normally be called an “interstitial” entity, and the second complex present, namely [Cu(NH₃)₄]²⁺. Cyanurate ribbons run parallel to each other in the extended structure, as seen in Figure 7. There are two independent interribbon spaces in the structure. One is bridged by the =Cu(NH₃)₂ moiety of the neutral complex [Cu(cyan)₂(NH₃)₂], in which the cyanurate is covalently bound to the copper. The next interribbon gap is bridged by the moiety [Cu(NH₃)₄]²⁺, which fits into an interstice in the three-dimensional structure. This copper center has a long bond to an *ortho*-carbonyl oxygen of the second cyanurate

present in the asymmetric unit. This cyanurate, which is an integral part of the cyanurate ribbon, has a dangling charge on its deprotonated imidate nitrogen atom.²⁶ Thus, the “unligated” cyanurate is part of what can be qualified as the most important structural feature in **6**, namely the ribbon, while the transition metals are bridges; and one of the transition metal complexes, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, can validly be called an interstitial moiety. This is just the opposite of the roles usually assumed by analogous entities in the descriptions of crystal structures of transition-metal complexes.

Still with respect to the structure of **6**, the available data do not permit a definitive conclusion as to why the crenelled ribbon of **5** forms first, and the linear ribbon of **6** only upon stronger treatment of **5**. We can speculate that the complex $\text{trans}[\text{Cu}(\text{cyan})_2(\text{NH}_3)_2]$ is the first product of its reaction that is both stable and sufficiently insoluble to precipitate. This product, **5**, crystallizes in a thermodynamically favorable structure with the crenelled ribbon. Under forcing conditions, the complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ forms, albeit slowly, and structure **6** precipitates preferentially. This proposed sequence of events carries the implicit conclusion that the structure of **6**, with the linear ribbon, is even more favorable thermodynamically than that of **5**.

Aggregation Modes of the Cyanurate Ribbon. Compounds **1–9** can be divided into three categories, depending on the manner in which they form their respective crystal structures. In the first category are the systems that are the expected products of their respective reactions and which crystallize without any other chemical entity present. These are the square copper complex $\text{trans}[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{NH}_3)_2]$ (**5**, with the crenelled ribbon), the trigonal-planar copper compound $[\text{Cu}(\text{cyan-}\kappa\text{N})(\text{PPh}_3)_2]$ (**9**), and the two octahedral nickel complexes, $\text{trans}[\text{Ni}(\text{cyan-}\kappa\text{N})_2(\text{NH}_3)_4]$ (**7**), and $[\text{Ni}(\text{cyan-}\kappa\text{N})_2(\text{NH}_3)_2(\text{H}_2\text{O})_2]$ (**8**).

In the second category we have the compounds that are chemically expected—or at least not surprising—products, but which crystallize in more complex structures accommodating the linear cyanurate ribbon. Compound **1**, the square copper complex $\text{trans}[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{H}_2\text{O})_2]$, is the expected product of its reaction; but it crystallizes with two formula units of Na(cyan) and four molecules of water, yielding a solid system with the cyanurate ribbon. The formation of the linear ribbon, at least within the confines of the rapidly formed structure type observed for **1**, would not be possible without the incorporation of the two units of Na(cyan), which bring two cyanurates to the ribbon.²⁷ An even more complex example is seen for **6**, $\text{trans}[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{NH}_3)_2]\text{trans}[\text{Cu}(\text{cyan-}\kappa\text{O}^2)_2(\text{NH}_3)_4]$ which as described above is formed only under stressing conditions and involves the incorporation of the interstitial fragment $[\text{Cu}(\text{NH}_3)_4]^{2+}$, which has weak bonds to its fifth and sixth coordination sites from two *ortho*-carbonyl oxygen atoms of cyanurate ions present in neighboring ribbons.

The third category of products consists of the previously reported complexes $[\text{M}(\text{cyan-}\kappa\text{N})(\text{H}_2\text{O})_5](\text{cyan})\cdot 2\text{H}_2\text{O}$, for M =

Mn (**2**), Co (**3**), and Ni (**4**). The cationic transition metal complexes formed in these cases are not the expected products; and even though the crystals possess the components necessary for the formation of what would be the expected neutral complexes, $\text{trans}[\text{M}(\text{cyan-}\kappa\text{N})_2(\text{H}_2\text{O})_4]$, one of the cyanurates participates in the cyanurate ribbon instead of bonding to the metal center. The formation of the cyanurate ribbon and of the richly hydrogen-bonded structure in the plane containing the ribbon is likely an important factor in these cases in establishing the nature of the transition-metal complex that is observed in the solid.

The cyanurate ribbon has qualitatively different chemical origins in the three categories of structures outlined above. In the first category, consisting in compounds **5** and **7–9**, the ribbon is the result of *self-assembly*, the process by which a small, initially formed moiety possessing appropriate topological information is aggregated into a larger, organized structure.^{28,29} All of the cyanurates are chemically equivalent, and all participate equally in the ribbon. In the compounds of the second category—namely, complexes **1** and **6**, which require the presence of auxiliary components in order to crystallize with the linear cyanurate ribbon—the cyanurates all still participate in essentially the same manner in the ribbon, but they are not chemically equivalent. Half of the cyanurate moieties are bound to transition metal centers, and half are unligated. The fundamental complexes, $\text{trans}[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{H}_2\text{O})_2]$ in **1** and the initially formed $\text{trans}[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{NH}_3)_2]$ of the multi-component **6** apparently do not alone possess the topological information necessary to give the linear ribbon under the constraints imposed by the presence of the transition metal and the other ligands. In order to render the aggregate structure, they require “helper molecules”, entities which bear no chemical relationship to the first products of the reactions, in the form of two equivalents of sodium cyanurate for **1** and a second complex in the case of **6**.

Although this second category possesses a ribbon equivalent at first sight to that formed by the first group of compounds, the nature of the assembly is distinct. If one treats the linear cyanurate ribbon as an isolated entity, it is the same in all cases. But if one considers the environment of the ribbon, the different chemical natures of alternate cyanurates (one bound to metal, one unbound) confer on the superstructure a second periodicity.

(27) (a) A recent report^{27b–d} describes a structure identified as $\text{trans}[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{H}_2\text{O})_2]$, which is reported with a unit cell, space group, and crenelled cyanurate ribbon identical to those of the analogous ammine complex, $\text{trans}[\text{Cu}(\text{cyan-}\kappa\text{N})_2(\text{NH}_3)_2]$, **5**, described in this study and in the papers by Taylor⁷ and by Slade *et al.*⁸ Our own efforts to obtain a crystalline material based on the aquacyanurate complex of copper(II) in the absence of sodium ion were fruitless, as were our attempts to crystallize the same complex in the presence of lithium, potassium, or tetra-*tert*-butylammonium. (b) Chen, C.-Z.; Shao, S.-B.; Huang, X.-Y.; Gao, D.-S.; Lin, Z.-B. *Jiegou Huaxue* **1995**, *14*, 356–358. (c) *Chem. Abstr.* **1996**, *124*, 20317r. (d) Crystal and structural data can be found in the Cambridge Structural Database,¹⁹ reference code ZETDOR.

(28) (a) Alberts, B.; Bray, D.; Lewis, J.; Raff, M.; Roberts, K.; Watson, J. D. *Molecular Biology of the Cell*; Garland Publishing, Inc.: New York, 1983. (b) For insight into the early concept of self-assembly, see: Watson, J. D. *Molecular Biology of the Gene*, 3rd ed.; W. A. Benjamin, Inc.: Menlo Park, CA, 1975; pp 108–109. (c) Butler, P. J. G.; Klug, A. *Sci. Am.* **1978**, *52*–59.

(29) See, for example, the following papers and references therein: (a) Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1838–1840. (b) Stang, P. J.; Olenyuk, B.; Fan, J.; Arif, A. M. *Organometallics* **1996**, *15*, 904–908. (c) Khan, M. I.; Meyer, L. M.; Haushalter, R. C.; Schweitzer, A. L.; Zubieta, J.; Dye, J. L. *Chem. Mater.* **1996**, *8*, 43–53. (d) MacDonald, J. C.; Whitesides, G. M.; *Chem. Rev.* **1994**, *94*, 2383–2420. (e) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Langford, S. J.; Menzer, S.; Prodi, L.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 978–981. (f) Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1995**, 1615–1627.

(26) (a) We are aware of only five structurally characterized (by X-ray diffraction) copper(II) complexes containing bonds to fifth or sixth and sixth ligands when four of the ligands are NH_3 , and in all cases the extra ligands are bound through oxygen or through neutral nitrogen. The fifth and sixth formation constants of Cu(II) are relatively small. These are $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})]^{2+}$ in $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{PF}_6)_2 \cdot (18\text{-crown-6})]^{2+}$, $\text{trans}[\text{Cu}(\text{O}_2\text{N}:\text{CC}(\text{CONH}_2)_2)_2(\text{NH}_3)_4]$,^{26c} $\text{trans}[\text{Cu}(\text{ethoxyacetato})_2(\text{NH}_3)_4]$,^{26d} $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]^{2+}$,^{26e} and $[\text{K}[\text{Cu}(\text{NH}_3)_5](\text{PF}_6)_3]$.^{26f} References b, c, and d were found using the Cambridge Structural Database.¹⁹ (b) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 849–850. (c) Chekhlov, A. N.; Yurtanov, A. I.; Martynov, I. V. *Koord. Khim.* **1987**, *13*, 1541–1544; *Chem. Abstr.* **1988**, *108*, 86830d. (d) Prout, K.; Mtetwa, V. S. B.; Rossotti, F. J. C. *Acta Crystallogr., Sect. B* **1993**, *B49*, 73–78. (e) Morosin, B. *Acta Crystallogr., Sect. B* **1969**, *B25*, 19–30. (f) Duggan, M.; Ray, N.; Hathaway, B. J.; Tomlinson, A. A. G.; Brint, P.; Pelin, K. *J. Chem. Soc., Dalton Trans.* **1980**, 1342–1348.

Table 3. Summary of Crystallographic Data for *trans*-[Cu(cyan- κ N)₂(H₂O)₂] \cdot 2Na(cyan) \cdot 4H₂O (**1**), *trans*-[Cu(cyan- κ N)₂(NH₃)₂] (**5**), *trans*-[Cu(cyan- κ N)₂(NH₃)₂]*trans*-[Cu(cyan- κ O²)₂(NH₃)₄] (**6**), *trans*-[Ni(cyan- κ N)₂(NH₃)₄] (**7**), [Ni(cyan- κ N)₂(NH₃)₂(H₂O)₂] (**8**), and [Cu(cyan- κ N)(PPh₃)₂] (**9**)^a

	1	5	6	7	8	9
formula	CuC ₁₂ H ₂₀ N ₁₂ O ₁₈ Na ₂	CuC ₆ H ₁₀ N ₈ O ₆	Cu ₂ C ₁₂ H ₂₆ N ₁₈ O ₁₂	NiC ₆ H ₁₆ N ₁₀ O ₆	NiC ₆ H ₁₄ N ₈ O ₈	CuC ₄₁ H ₃₂ N ₃ P ₂ O ₃ Cl ₆ D ₂
color	blue	dark blue	dark blue	violet	blue-violet	colorless
fw	729.88	353.76	741.59	382.71	384.54	956.89
<i>T</i> (°C)	26(1)	24(1)	26(1)	25(2)	25(1)	25(1)
crystal system	triclinic	triclinic	triclinic	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	<i>Cmcm</i>	<i>P2₁/m</i>	$P\bar{1}$
<i>a</i> (Å)	6.7552(8)	5.031(1)	7.143(1)	12.050(2)	6.334(1)	11.645(1)
<i>b</i> (Å)	10.455(1)	6.989(1)	8.683(2)	7.266(2)	16.022(2)	13.440(2)
<i>c</i> (Å)	10.445(1)	9.120(2)	11.602(2)	15.971(2)	7.017(1)	16.561(2)
α (deg)	62.819(6)	90.04(3)	102.12(3)	90	90	102.051(8)
β (deg)	71.815(6)	98.01(3)	101.24(3)	90	114.13(2)	97.585(9)
γ (deg)	83.688(5)	110.84(3)	106.22(3)	90	90	113.132(9)
<i>V</i> (Å ³)	623.0(1)	296.3(3)	650.44(3)	1398.3(2)	650.0(2)	2264.2(4)
<i>Z</i>	1	1	1	4	2	2
q.o.f. ^b	1.113	1.180	1.121	1.158	1.029	1.078
R1, ^c wR2 ^d	0.0319, 0.0779	0.0265, 0.0730	0.0813, 0.3060	0.0265, 0.0750	0.0410, 0.1056	0.0685, 0.1227

^a All data with $F_o^2 \geq -3\sigma(F_o^2)$ were used in the refinements of **1** and **5**; and all positive data were used for **6–9**. ^b Quality of fit = $[\sum w(F_{obs}^2 - F_{calc}^2)^2 / \sum (N_{obs} - N_{params})]^2$. ^c $R1 = \sum ||F_{obs}| - |F_{calc}|| / \sum |F_{obs}|$. ^d $wR2 = [\sum w(F_{obs}^2 - F_{calc}^2)^2 / \sum w(F_{obs}^2)]^{1/2}$.

Alternate cyanurates in the ribbon, although locally equivalent in the superstructure, are chemically different.

We are not aware of the existence of distinguishing terminology for aggregate structures that are internally structurally homogeneous but chemically heterogeneous. We are disinclined to use the unmodified term *self-assembly* for the ribbon in the second group of compounds, since no individual chemical entity present possesses all of the topological information necessary for the formation of the aggregate.

Complexes of the third category, consisting of **2–4**, give rise to a cyanurate ribbon essentially identical to that of the second category just discussed. For **2–4**, however, it is probable that part of the chemical environment of one component of the ribbon—namely the pentaqua complex of which the ligated cyanurate is part—is not a thermodynamically favored product, and that the stability of the crystal structure is the deciding factor in the rapid crystallization of the transition-metal complex isolated.

Conclusion

All of the solids formed by compounds **1–9** have extended three-dimensional structures that are stabilized by intermolecular interactions—principally hydrogen bonds and cyanurate stacking. Except for the cases of the isostructural systems **2–4**, and the qualitatively similar structures **7** and **8**, however, the only feature that all of the structures have in common is the cyanurate ribbon, which is linear in eight of the systems and crenelled in one. The geometrical parameters of the cyanurate ribbons, moreover, are strikingly similar in all of the systems, as seen in Table 2.

We conclude, then, that the cyanurate ribbon—an aggregate structure held together by hydrogen bonding and formed by self-assembly in some of its occurrences and not in others—is a significant, even determinative, entity in the structural chemistry of coordination complexes of isocyanurate. The formation of the aggregate is a predictive factor in this chemistry, alongside the usual considerations of the types of coordination normally seen for particular d-block elements.

Experimental Section

Instrumentation. Elemental analyses of C, H, and N were performed on a Perkin-Elmer microanalyzer model 240B. Infrared spectra were recorded in the range of 4000 to 200 cm⁻¹ from Nujol mulls between polystyrene films on Perkin Elmer 883 and FT1730 spectrophotometers. Mass spectrometry for **9** was carried out on a VG Autospec using the FAB technique in 3-nitrobenzyl alcohol.

Molecular weight measurements in solution were performed for **9** on a Knauer vapor pressure osmometer.

Syntheses. *trans*-[Cu(cyan- κ N)₂(H₂O)₂] \cdot 2Na(cyan) \cdot 4H₂O (**1**). To a suspension of Na(cyan) (0.1921 g, 1.272 mmol) in 60 mL of a mixture of *i*-PrOH and H₂O (4/1) was added a solution of CuCl₂ \cdot 2H₂O (0.0362 g, 0.212 mmol) in 15 mL of *i*-PrOH. The resulting pale blue suspension was refluxed for 6 h. During this time, a violet-colored solid precipitated. At the end of the reaction, the suspension was filtered at reflux temperature, and the solid was dried *in vacuo*. Obtained: 0.121 g (78% yield). Anal. Calcd for C₁₂H₂₀CuN₁₂Na₂O₁₈ (729.88): C, 19.74; H, 2.76; N, 23.02. Found: C, 19.85; H, 2.59; N, 23.16. IR (cm⁻¹): 3542 (s), 3480 (s), 3250 (broad, m), 1773 (m), 1741–1602 (broad, vs), 1264 (m), 1118 (w), 1102 (w), 1018 (w), 842 (m), 850 (m), 564 (s), 473 (m), 456 (m). Crystals suitable for X-ray measurements were obtained by slow diffusion of a dilute solution of Na(cyan) in EtOH/H₂O into a concentrated solution of CuCl₂ \cdot 2H₂O in *i*-PrOH, at room temperature, over a period of 15 days.

[M(cyan- κ N)(H₂O)₅](cyan) \cdot 2(H₂O) (M = Mn (**2**), Co (**3**), Ni (**4**)). The preparations and crystallographic characterizations of these compounds were described in a previous report.⁴

trans-[Cu(cyan- κ N)₂(NH₃)₂] (**5**). CuCl₂ \cdot 2H₂O (0.4 g, 2 mmol) and Hcyan in ratio 1:2 were dissolved in boiling water (50 mL) with stirring. To the mixture was added, dropwise, an excess of concentrated aqueous NH₄OH, until the blue product precipitated. Good quality crystals can be obtained from the mother liquor, upon cooling. Yield: 0.54 g (89%). Anal. Calcd for C₆H₁₀CuN₈O₆: C, 20.37; H, 2.85; N, 31.68. Found: C, 20.74; H, 2.73; N, 31.38. IR (cm⁻¹): 3340 (vs), 3285 (vs), 3272 (vs), 1787 (m), 1739 (vs), 1701–1640 (broad, vs), 1254 (vs), 1088 (s), 1010 (m), 823 (m), 780 (s), 691 (m), 592, (m), 556(s), 456 (m), 433 (m).

trans-[Cu(cyan- κ N)₂(NH₃)₂]*trans*-[Cu(cyan- κ O²)₂(NH₃)₄] (**6**). A solid sample, which at the outset consisted of pure [Cu(cyan- κ N)₂(NH₃)₂] (**5**) was recrystallized several times (4 or 5 times in various preparations) from concentrated aqueous ammonia. The small twinned crystals obtained are *trans*-[Cu(cyan- κ N)₂(NH₃)₂]*trans*-[Cu(cyan- κ O²)₂(NH₃)₄] (**6**). The yield is quantitative. IR (cm⁻¹): 3351 (s), 3179 (s), 1898 (m), 1784 (s), 1738–1543 (broad, vs), 1255 (s), 1225 (s), 1113 (m), 1098 (m), 930–822 (broad, m), 591 (m), 558 (s), 540 (m), 477 (d), 457 (m), 430 (s).

trans-[Ni(cyan- κ N)₂(NH₃)₄] (**7**). NiBr₂ (0.2 g, 0.9 mmol) and Hcyan (0.24 g, 1.8 mmol) were dissolved in boiling water (30 mL). To the hot stirring solution was added 4 mL of concentrated aqueous NH₄OH (28% NH₃ by weight). The solution turned blue-violet, and a violet solid precipitated after 2 days at 3 °C. After the initial precipitate had been filtered, violet crystals were obtained from the mother liquor after it had been kept at 3 °C for 1 week. Complex **7**, when heated, turns pink at 184 °C, and decomposes without melting above 400 °C. Yield: 0.15 g (43%). Anal. Calcd for C₆H₁₆N₁₀NiO₆: C, 18.82; H, 4.21; N, 36.58. Found: C, 18.90; H, 4.05; N, 36.31. IR (cm⁻¹): 3396

(m), 3150 (s), 1773 (m), 1723 (s), 1682–1409 (vs), 1372 (vs), 1137 (s), 834 (m), 550 (s), 467 (m), 422 (m). In addition to the room-temperature structure determination that we report here for **7**, we have observed a nondestructive phase transformation that leads to structural distortion with changes of temperature. A full study of this system is now in progress, and will be reported separately.

(OC-6-33)-[Ni(cyan-κN)₂(NH₃)₂(H₂O)₂] (8). A sample of *trans*-[Ni(cyan-κN)₂(NH₃)₄] (**7**) was suspended in H₂O (10 mL) and heated to 100 °C for several hours, during which the violet color of complex **7** evolved to the blue color of the product. Blue, block-shaped crystals were obtained by slowly cooling the reaction solution. Crystalline samples of much poorer quality can be obtained by crystallizing the product *trans*-[Ni(cyan-κN)₂(NH₃)₄] in open air. Anal. Calcd for C₆H₁₄N₈NiO₈: C, 18.49; H, 3.62; N, 29.75. Found: C, 19.17; H, 3.62; N, 30.30. IR (cm⁻¹): 3394 (m), 3292 (m), 1784 (m), 1730 (s), 1688 (s), 1599 (broad, vs), 1379 (vs), 1229 (m), 1083 (w), 850 (m), 785 (s), 557 (s), 481 (m), 434 (m).

[Cu(cyan-κN)(PPh₃)₂]₂·2CDCl₃ (9). To a colorless solution of 0.10 g (0.15 mmol) of Cu(PPh₃)₂(NO₃) in 30 mL of CH₂Cl₂ was added 0.056 g of NBu₄(cyan) (1:1 ratio). The solution was stirred for 2 h, whereupon the solvent was removed *in vacuo*. The resulting white powder was treated with *i*-PrOH in order to dissolve the NBu₄NO₃. The remaining white powder was isolated, washed with *n*-pentane and dried. Yield: 0.10 g (93%). Anal. Calcd (for [Cu(cyan-κN)(PPh₃)₂]) C₃₉H₃₂CuN₃O₃P₂: C, 65.41; H, 4.5; N, 5.87. Found: C, 64.03; H, 4.01; N, 5.01. The discrepancy between the calculated and observed analyses is probably caused by the presence of a small amount of CH₂Cl₂. The analyses fit if the calculated values include 0.25 CH₂Cl₂, and the X-ray structure shows that the compound crystallizes with solvent. IR (cm⁻¹): 1731 (m), 1689 (m), 1610 (s), 1379 (s), 1310 (w), 1276 (m), 1096 (m), 1024 (w), 784 (m), 742 (m), 695 (s), 544 (m), 521 (s), 505 (s). Mass spectrometry: 325 (100) [Cu(PPh₃)₂]⁺, 587 (100) [Cu(PPh₃)₂]⁺. Molecular weight in solution: found, 712 amu; calcd, 716 amu. Crystals of good quality but unstable due to solvent loss can be obtained by slow diffusion of *n*-pentane into a dilute solution of the complex in a mixture of CH₂Cl₂ and CHCl₃ at 3 °C. More stable crystals were isolated from an NMR tube containing a solution of **9** in CDCl₃, which had been allowed to rest for 72 h at -18 °C.

X-ray Structure Determinations. Data collection for complexes **1**, **6**, and **7** were performed at room temperature on a Siemens-STOE AED2 four-circle diffractometer.³⁰ Complexes **5**, **8**, and **9** were analyzed using a Nonius CAD-4 diffractometer,³¹ also at room temperature. In all cases, unit cell parameters were obtained by indexation of 25 reflections and refined by least-squares fits to a set of from 25 to 70 carefully centered reflections, chosen from different regions of recipro-

cal space. Intensity data were corrected for Lorentz and polarization effects. For each data set, an absorption correction was applied, based on ψ -scans and, in cases of suitable Laue symmetry, on measurements of equivalent reflections.³² The structures were solved by either Patterson or direct methods and refined to F_o^2 using full-matrix least-squares.³³ Except for the structure of compound **6**, which was determined from a twinned crystal, all non-hydrogen atoms were treated as anisotropic. Also with the exception of **6**, hydrogen atoms were located in difference electron density maps and refined either freely or riding on their parent atoms, depending on their behavior under unconstrained refinement. The treatment of data for the twinned crystal of **6** is described in the Supporting Information. A summary of the more important crystallographic parameters and least-squares residuals for all of the structure determinations is given in Table 3.

Centric space groups were chosen in all cases on the basis of maximal symmetry descriptions of the structural patterns present. The structures of **1**, **5**, **6**, and **9** are triclinic, and the centric group $P\bar{1}$ was chosen for all, rather than the acentric $P1$. For **7**, the centric group $Cmcm$ gives a full description of the symmetry present, rather than either of the acentric groups $Cmc2_1$ or $C2cm$. For **8**, the same considerations led to a choice of $P2_1/m$ over the acentric group $P2_1$, which has the same systematic absences.

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Supporting Information Available: For the crystal structures of compounds **1**, **5**, **6**, **7**, **8**, and **9**, tables of crystallographic data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters are available, as is a description of the treatment of the twinning for the determination of the crystal structure of **6** (39 pages). An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering information and Internet access instructions.

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(32) Diffraction data were processed on a Local Area VAXcluster (VAX/VMS V5.5-2) with the commercial package SHELXTL-PLUS Release 4.21/V, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990; on an AlphaStation 200 4/166 (OpenVMS Alpha V6.2) with SHELXTL Ver. 5.05/VMS, Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996; and on a Hewlett-Packard 9000 Model 715/50 (HP-UX V9.01 and V9.05).

(33) (a) Structure solution: Sheldrick, G. M. SHELXS-86, FORTRAN program for crystal structure solution, University of Göttingen, 1986. (b) Structure refinement: Sheldrick, G. M. SHELXL-93, FORTRAN program for crystal structure refinement, University of Göttingen, 1993. (c) Structure refinement: SHELXL-96, FORTRAN program for crystal structure refinement, beta test version: 1996, George M. Sheldrick.

(30) (a) AED-4 control program: DIF4 (Stoe & Cie. GmbH, Darmstadt, Germany). (b) AED-4 data reduction: REDU4 Rev. 7.03. (Stoe & Cie. GmbH, Darmstadt, Germany).

(31) (a) CAD-4 control program: CAD4-PC Version 1.5c; Delft Instruments X-ray Diffraction bv: Delft, The Netherlands, 1994. (b) CAD-4 data reduction: XCAD4B (K. Harms, private communication, 1994).