

Syntheses and Solid-State Structures of Molecular and Extended Silver(I) Complexes of 4-Isocyano-3,5-diisopropylbenzonitrile

Ming-Xing Li,^{*,1} Kung-Kai Cheung,^{*,2} and Andreas Mayr^{†,2}

^{*}Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China; and

[†]Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York, 11794-3400

DEDICATED TO PROF. W. P. FEHLHAMMER ON THE OCCASION OF HIS 60TH BIRTHDAY

The molecular complexes $[\text{Ag}(4\text{-CN-3,5-}i\text{-Pr}_2\text{-C}_6\text{H}_2\text{CN})_2]\text{X}$, **1** (a, X = BF₄; b, X = SO₃CF₃), have been prepared by reaction of the respective silver(I) salts with 2 equivalents of the isocyanide in benzene solution. Reaction of **1b** with an equivalent amount of AgSO₃CF₃ in benzene solution gave the extended molecular solid $\{[\text{Ag}(4\text{-CN-3,5-}i\text{-Pr}_2\text{-C}_6\text{H}_2\text{CN})_2]\text{SO}_3\text{CF}_3\}_n$, **2**. The solid-state structures of **1a** and **2** have been determined by single-crystal X-ray crystallography. Compound **1a** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.506(2)$ Å, $b = 12.838(2)$ Å, $c = 12.974(2)$ Å, $\alpha = 100.65(2)^\circ$, $\beta = 101.52(2)^\circ$, $\gamma = 105.37(2)^\circ$, $V = 1600.1(7)$ Å³, and $Z = 2$ with $R = 0.056$ and $wR = 0.087$. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.6868(8)$ Å, $b = 10.551(1)$ Å, $c = 11.559(1)$ Å, $\alpha = 76.350(9)^\circ$, $\beta = 82.037(9)^\circ$, $\gamma = 71.481(9)^\circ$, $V = 1086.0(4)$ Å³, and $Z = 1$ with $R = 0.027$ and $wR = 0.036$. Compound **1a** may be described as a dicoordinate silver(I) complex with a significantly bent linear coordination geometry (C–Ag–C 156.1(2)°). The bending of the diisocyanide metal group is caused by the interaction with the BF₄ anion (shortest Ag–F distance 2.534(8) Å). The nitrile groups in **1b** are not engaged in any directional intermolecular interaction. The solid-state structure of **2** consists of linear chains of $[\text{Ag}(4\text{-CN-3,5-}i\text{-Pr}_2\text{-C}_6\text{H}_2\text{CN})_2]\text{SO}_3\text{CF}_3$ units, whereby each silver ion is coordinated to one isocyano group and one nitrile group of consecutive cyanoisocyanoarene ligands. These linear chains are arranged in antiparallel fashion to form infinite sheets. Within the sheets, the silver ions of pairs of chains are pulled near each other by electrostatic interactions with the SO₃CF₃ anions. These double chains are held together primarily by π interactions of the cyanoisocyanoarene groups. © 2000 Academic Press

Key Words: silver(I); isocyanobenzonitrile; metal complex; one-dimensional coordination polymer.

INTRODUCTION

Coordination polymers (1) are a promising class of solid-state molecular material. By proper choice of metal center

¹Permanent address: Department of Chemistry, Fudan University, Shanghai, People's Republic of China.

²To whom correspondence should be addressed. K.-K.C.: E-mail kkcheung@hkucc.hku.hk. AM.: fax +1-516-632-7960; e-mail amayr@notes.sc.sunysb.edu.

and polytopic ligand, it is possible to exert considerable control over the electronic and steric properties (2). As far as the dimensionality and the dimensions of the solid-state structures are concerned, the primary steric information is usually contained in the polytopic organic ligands (3). As an alternative approach toward the design of one-, two-, and three-dimensional coordination polymers, we (4) are utilizing linear functionalized isocyanide ligands (5) and the intrinsic coordination geometries of various transition metal isocyanide complexes (6). Because of the propensity of silver(I) to form linear dicoordinate metal complexes and the kinetic lability of many silver(I)–ligand interactions, it appeared promising to attempt the synthesis of crystalline low-dimensional solids from functionalized isocyanide silver(I) complexes. Silver(I) salts have previously been demonstrated to form coordination polymers based on bis(isocyanide)- (7) as well as bis(nitrile)silver units (8). Therefore, it appeared to be of interest to explore the coordination chemistry of cyanoisocyanoarenes and silver(I) salts. Here we report the formation of discrete bis(isocyanide) complexes and a one-dimensional coordination polymer from 4-isocyano-3,5-diisopropylbenzonitrile and Ag(I) salts (see Scheme 1).

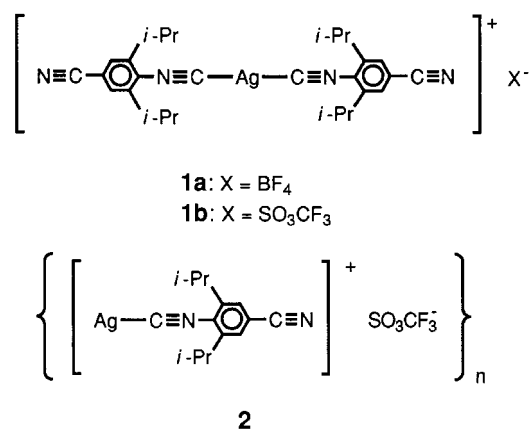
EXPERIMENTAL

3,5-Diisopropyl-4-isocyanobenzonitrile was prepared as described in the literature (9). Benzene, tetrahydrofuran, ether, and CH₂Cl₂ were distilled under N₂ from appropriate drying agents. All other solvents and reagents were used as received from commercial sources. All synthetic procedures were performed under an atmosphere of N₂. The ¹H NMR spectra were recorded at 300 MHz.

$[\text{Ag}(4\text{-CN-C}_6\text{H}_2\text{-3,5-}(i\text{-C}_3\text{H}_7)_2\text{-CN})_2](\text{BF}_4) \cdot (\text{C}_6\text{H}_6)_{0.5}$, **1a**

AgBF₄ (48.7 mg, 0.25 mmol) is dissolved in 20 ml of dichloromethane. 4-CN-C₆H₂-3,5-(*i*-C₃H₇)₂-CN (106.2 mg,





SCHEME 1

0.5 mmol) is added. The solution is stirred for 12 hr. The solution is reduced to about 5 ml and 20 ml of diethyl ether is added to afford a white precipitate, which is filtered off and washed with diethyl ether. Yield: 103 mg, 59%. This product is dissolved in benzene. Upon slow evaporation, colorless crystals form. $^1\text{H NMR}$ (CDCl_3): δ 7.54 (s, 4 H), 7.37 (s, 3 H, benzene), 3.39 (h, 4 H), 1.34 (d, 24 H). IR (cm^{-1}): CH_2Cl_2 ; 2233(w), 2192(s); KBr, 3077 (w), 2968 (m), 2932 (w), 2875 (w), 2232 (w), 2192 (m), 2160 (w), 1577 (w), 1465 (m), 1280 (w), 1077 (br, vs), 889 (w), 762 (w), 712 (m), 628 (w).

$[\text{Ag}(4\text{-CN-C}_6\text{H}_2\text{-3,5-(i-C}_3\text{H}_7)_2\text{-CN})_2](\text{SO}_3\text{CF}_3)$, **1b**

AgSO_3CF_3 (128.5 mg, 0.5 mmol) is dissolved in 5 ml of benzene. A benzene solution (5 ml) of 212 mg (1.0 mmol) of $\text{CN-C}_6\text{H}_2(\text{C}_3\text{H}_7)_2\text{-CN}$ is added with stirring. Within a few minutes, a white precipitate forms. The mixture is stirred for 12 hr. The solid is filtered off and washed with diethyl ether. Yield: 260 mg, 76%. IR (cm^{-1}): CH_2Cl_2 , 2237 (w), 2189 (s); KBr, 3076 (w), 2968 (m), 2929 (w), 2873 (w), 2232 (w), 2200 (s), 2162 (w), 2123 (w), 1578 (w), 1460 (m), 1253 (br, s), 1154 (s), 1029 (s), 763 (w), 636 (s).

$\{[\text{Ag}(4\text{-CN-C}_6\text{H}_2\text{-3,5-(i-C}_3\text{H}_7)_2\text{-CN})](\text{SO}_3\text{CF}_3)\}_n$, **2**

$[\text{Ag}(4\text{-CN-C}_6\text{H}_2\text{-3,5-(i-C}_3\text{H}_7)_2\text{-CN})_2](\text{SO}_3\text{CF}_3)$ (68.2 mg, 0.1 mmol) is dissolved in 20 ml of dichloromethane. A benzene solution (10 ml) of AgSO_3CF_3 (51.4 mg, 0.2 mmol) is added. The solution is stirred for 12 hr, and then allowed to stand in an atmosphere of diethyl ether. Colorless crystals form. The product is filtered off and washed with diethyl ether. Yield: 15 mg, 32%. IR (KBr, cm^{-1}): 3076 (w), 2968 (m), 2931 (w), 2876 (w), 2262 (w), 2187 (m), 1578 (w), 1468 (m), 1254 (br, s), 1166 (s), 1018 (s), 688 (m), 640 (s), 519 (m).

X-Ray Crystallographic Studies

The diffraction data for compound **1a** were collected on an MAR imaging plate detector system with graphite-

monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and an MAR X-ray generator (50 kV and 50 mA) using $3^\circ \phi$ -oscillation and a detector-to-crystal distance of 120 mm and 270 s exposure. Reflections from 70 images were interpreted and intensities integrated using the program DENZO (10). From 16,173 measured reflections, 5437 unique reflections were obtained ($R_{\text{int}} = 0.027$), and the data were corrected for Lorentz and polarization effects.

The diffraction data for complex **2** were collected on a Rigaku AFC7R diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and a rotating anode X-ray generator (50 kV and 160 mA), ω - 2θ scan mode, 4060 reflections measured, 3834 unique ($R_{\text{int}} = 0.019$), data corrected for Lorentz and polarization effects, and an empirical absorption based on azimuthal scans of five strong reflections (minimum and maximum transmission factors 0.973 and 1.000).

The structure determinations and numerical calculations were done using the MSC crystal structure analysis package TeXsan (11), using a Silicon Graphics computer, and the full-matrix least-squares refinements were on F using reflections with $I > 3\sigma(I)$.

TABLE 1
Crystal and Data Collection Parameters for Complexes **1a**
and **2**

	1a	2
Formula	$\text{C}_{31}\text{H}_{35}\text{BN}_4\text{F}_4\text{Ag}$	$\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_6\text{F}_6\text{Ag}_2$
Formula weight	658.32	1016.57
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a , \AA	10.506(2)	9.6868(8)
b , \AA	12.838(2)	10.551(1)
c , \AA	12.974(2)	11.559(1)
α , deg	100.65(2)	76.350(9)
β , deg	101.52(2)	82.037(9)
γ , deg	105.37(2)	71.481(9)
V , \AA^3	1600.1(7)	1086.0(4)
Z	2	1
T , K	301	301
Crystal color	Colorless	Colorless
Crystal dimensions, mm \times mm \times mm	0.25 \times 0.20 \times 0.10	0.25 \times 0.10 \times 0.10
d (calcd), g cm^{-3}	1.366	1.554
μ , cm^{-1}	6.77	10.66
2θ max, deg		50
Unique reflections	5437	3834
Reflections ($I > 3\sigma(I)$) used in LS refinement	4412	2551
No. of variables	357	253
R	0.056 ^a	0.027 ^a
wR	0.087 ^{b,c}	0.036 ^{b,d}
(Δ/σ) max	0.05	0.03
Goodness of fit	2.74	1.23
$\Delta\rho$, e\AA^{-3}	-0.81/1.30	-1.10/1.24

^a $R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$, $w = 4F_o^2 / \sigma^2(F_o^2)$. ^c $\sigma^2(F_o^2) = \sigma^2(I) + (0.042F_o^2)^2$. ^d $\sigma^2(F_o^2) = \sigma^2(I) + (0.030F_o^2)^2$.

Hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were included in the calculations, but not refined. Crystal and data collection parameters for complexes **1a** and **2** are summarized in Table 1.

RESULTS AND DISCUSSION

Synthesis and Characterization

The silver(I) bis-isocyanide complexes **1a** and **1b** have been prepared by adding 2 equivalents of 4-isocyano-3,5-diisopropylbenzotrile to AgBF_4 and AgSO_3CF_3 , respectively, in benzene solution. The isocyanide group is a significantly stronger coordinating group than the nitrile group. As expected, only the formation of isocyanide metal complexes, not nitrile complexes, was observed. The coordination of the isocyanide group to the silver(I) center causes a characteristic shift (about 75 cm^{-1}) of the isocyanide $\text{C}\equiv\text{N}$ IR stretching frequency of the free ligand (2115 cm^{-1} in CH_2Cl_2) to higher wavenumbers, while the stretching frequency of the nitrile group (2233 cm^{-1}) remains essentially unchanged. In the solid phase (KBr), at least two IR absorptions are observed for the isocyanide groups of **1a**

and **1b**. The appearance of two isocyanide stretching frequencies for **1a** in the solid phase can be explained by the bending of the NC-Ag-CN group in the crystal structure (see below). The extended solid **2** was obtained by addition of a benzene solution of AgSO_3CF_3 to a methylene chloride solution of **1b**, and slow further addition of diethyl ether. The expected outcome of this reaction was a one-dimensional solid in which intact molecular units **1b** are connected by silver(I) ions via the nitrile groups. Coordination of the nitrile groups to Ag(I) in **2** is indicated by an increase of the nitrile $\text{N}\equiv\text{C}$ stretching frequency by 30 cm^{-1} (KBr), and the observed product is indeed a one-dimensional solid. However, all isocyanobenzotrile ligands within the individual extended chains are oriented in the same direction (see below). Thus the identity of the molecular building blocks **1b** is lost in solid **2**. The formation of **2** implies that the Ag-C bonds in **1b** are kinetically labile. In contrast to this situation, transition metal-isocyanide bonds are normally kinetically stable, a fact which we have utilized toward the formation of geometrically well-defined building blocks for coordination polymers (4, 9) and discrete open molecular structures (12). The kinetic lability of silver-isocyanide bonds is also apparent from the formation of crystalline

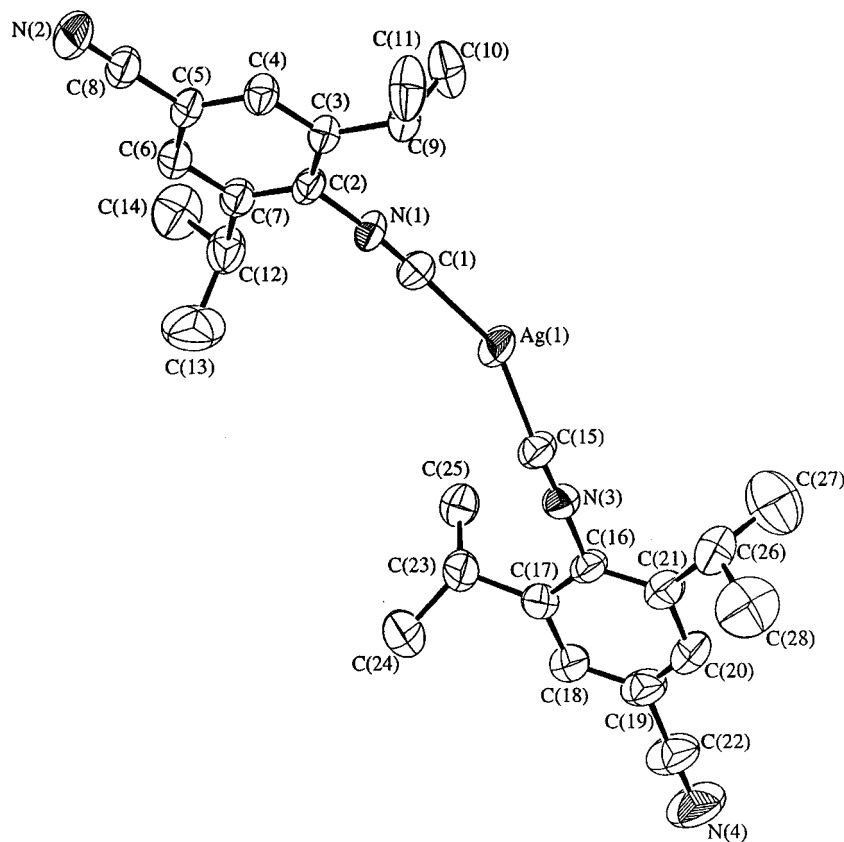


FIG. 1. ORTEP drawing of the cation of compound **1a**. The thermal ellipsoids are shown at the 40% probability level.

coordination polymers from silver(I) salts and diisocyanomethane (7).

Structures

The crystal structures of **1a** and **2** were determined by single-crystal X-ray crystallography. Drawings of the metal complex units of **1a** and **2** with the atomic numbering schemes are shown in Figs. 1 and 2. Selected bond lengths and bond angles are listed in Table 2.

Complex **1a** may be described as a two-coordinate silver(I) complex with a strongly distorted linear coordination geometry. The isocyanide ligands are coordinated to the silver center with an average Ag–C bond distance of 2.09 Å. The angle between the two isocyanide ligands, C(1)–Ag(1)–C(15), deviates by almost 24° from linearity. This distortion from linearity is caused by the interaction of the cationic silver center with the tetrafluoroborate anion. The shortest Ag–F distance, Ag(1)–F(1*) at 1 – x, – y, – z, is 2.534(8) Å, slightly longer than the Ag–F distances in AgF and Ag₂F (2.46 and 2.45 Å) (13). It may be concluded that the interaction between the cation and the anion is primarily electrostatic in nature. The crystal structure of **1a** consists of

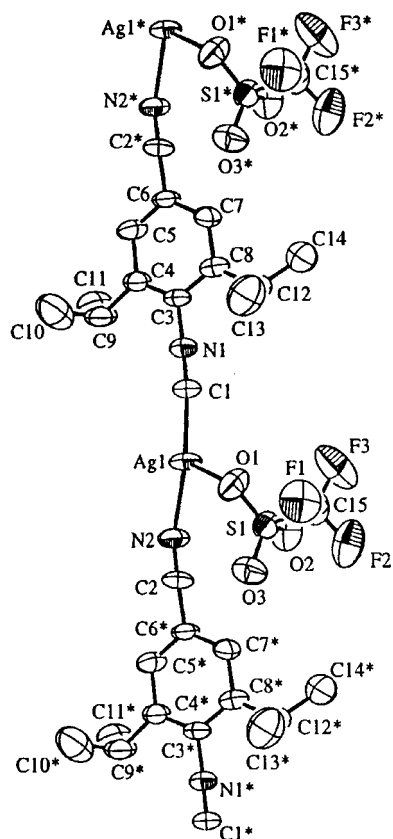


FIG. 2. ORTEP drawing of two molecular units of compound **2**. The thermal ellipsoids are shown at the 30% probability level.

TABLE 2
Selected Bond Lengths (Å) and Bond Angles (°) for
(a) Complex **1a** and (b) Complex **2**

(a) Complex 1a			
Ag(1)–C(1)	2.098(5)	Ag(1)–C(15)	2.092(5)
N(1)–C(1)	1.125(6)	N(3)–C(15)	1.128(6)
N(1)–C(2)	1.421(5)	N(3)–C(16)	1.419(6)
N(2)–C(8)	1.140(6)	N(4)–C(22)	1.129(8)
C(1)–Ag(1)–C(15)	156.1(2)	Ag(1)–C(1)–N(1)	176.6(5)
Ag(1)–C(15)–N(3)	174.0(4)	C(1)–N(1)–C(2)	176.2(5)
C(15)–N(3)–C(16)	177.3(5)		
(b) Complex 2			
Ag(1)–C(1)	2.076(3)	Ag(1)–N(2)	2.194(3)
Ag(1)–O(1)	2.478(3)	N(1)–C(1)	1.137(4)
N(1)–C(3)	1.413(4)	N(2)–C(2)	1.132(4)
C(2)–C(6)* ^a	1.446(5)	S(1)–O(1)	1.443(3)
S(1)–O(2)	1.419(3)	S(1)–O(3)	1.430(3)
N(2)–Ag(1)–C(1)	147.4(1)	Ag(1)–C(1)–N(1)	172.5(3)
Ag(1)–N(2)–C(2)	159.7(3)	C(1)–N(1)–C(3)	176.6(4)
N(2)–C(2)–C(6)	175.6(5)	Ag(1)–O(1)–S(1)	117.3(2)

^aC(6*) at 1 + x, – 1 + y, z.

interdigitated stacks of bis(arylisocyanide)silver complexes, whereby the BF₄ anions are located alternately on opposite sides of the stacks (Fig. 3). Because of the overlap of the aromatic π systems of adjacent rows of metal complexes, the repeat distance between the silver atoms is 6.6401(8) Å, which is about twice the typical π stacking distance of aromatic compounds. The space between the interdigitating phenyl rings and the bis(isocyanide)silver groups is filled by a benzene molecule of crystallization. The distances between the silver atom Ag(1) and the three nearest benzene carbon atoms, C(29*), C(30*), and C(31*) at – x, – y, – z, are 3.22(1), 2.955(8), and 3.33(1) Å, respectively. These distances are significantly longer than the shortest Ag–C contacts in AgClO₄·C₆H₆ (2.50 and 2.63 Å) (14).

Compound **2** is a one-dimensional solid. The crystal structure is made up of linear chains of [Ag(4-CN–C₆H₂–3,5–(i-C₃H₇)₂–CN)₂](SO₃CF₃) units. Each silver atom is connected to one isocyanide group and one nitrile

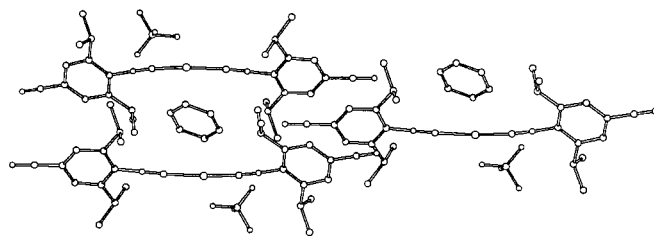


FIG. 3. Segment of the crystal structure of **1a** showing the interdigitation of the phenyl rings and the sandwiching of the enclosed benzene molecule between two silver atoms.

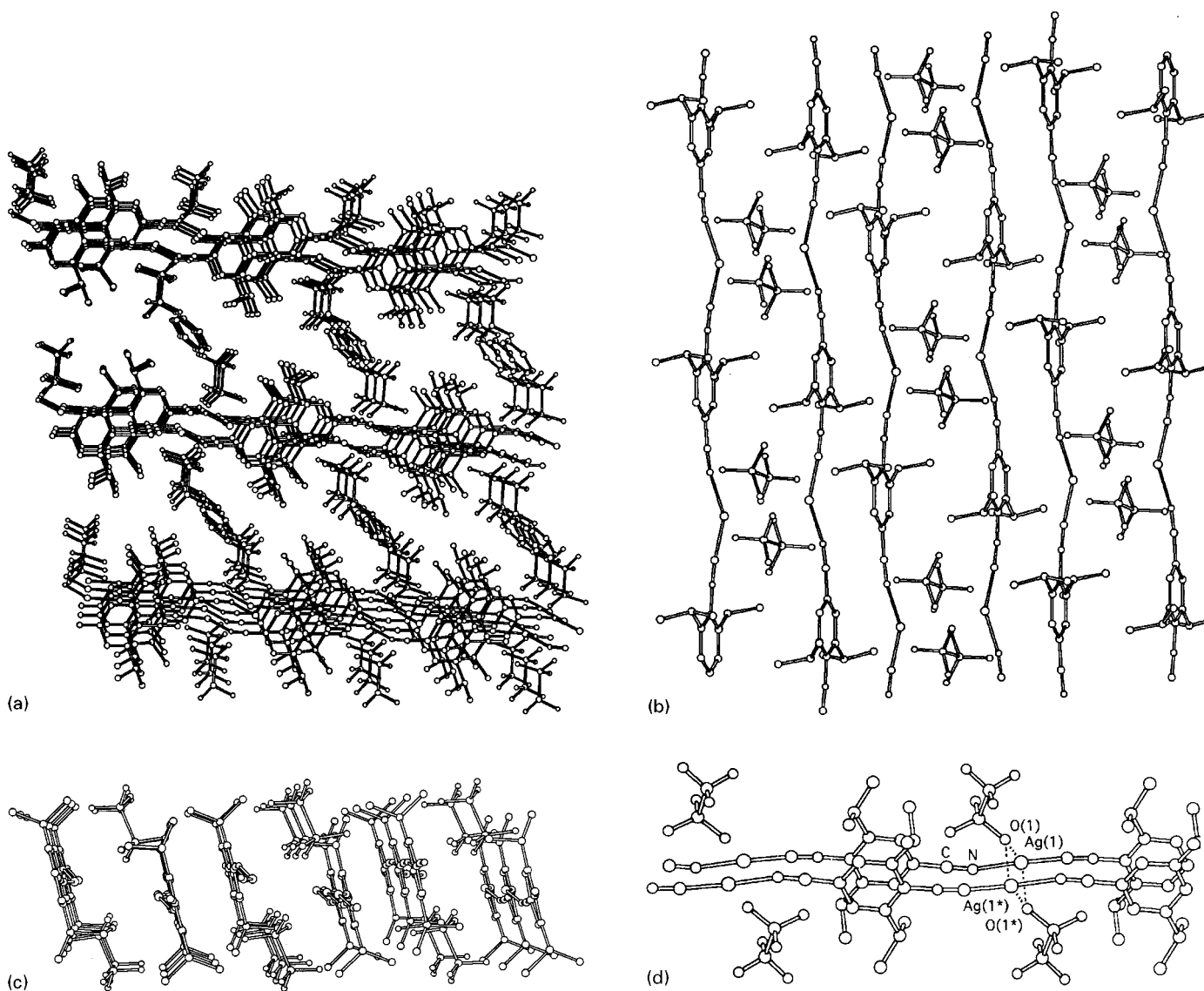


FIG. 4. Views of segments of the crystal structure of **2**. (a) Segment of three layers viewed along the *a* axis. (b) Segment of a single layer viewed approximately along the *c* axis. (c) View of the segment shown in (b) viewed approximately along the *a-b* vector. (d) Portion of a double chain highlighting the interactions between the silver and triflate ions.

group of two consecutive bridging ligands (Ag(1)–C(1) 2.076(3) Å and Ag(1)–N(2) 2.194(3) Å). Thus within a single chain, the cyanoisocyanoarenes all point in the same direction (Fig. 2). The chains are organized into layers (Fig. 4a), whereby adjacent chains are running in opposite directions. Within the layers, pairs of chains are held together by electrostatic interactions between the silver ions and the triflate ions. The flanking sides of these double chains are engaged in π stacking interactions. The segment of a single layer shown in Fig. 4b includes three double chains with two π stacking interfaces. The most conspicuous local structural feature within the double chains is the presence of pairs of silver atoms which are pulled toward each other by the

electrostatic influence of the triflate ions (Ag(1)–Ag(1*) at $-x, -y, 1-z, 4.050(1)$ Å). When the same segment is viewed along the direction of the chains (Fig. 4c), one can clearly discern that the aromatic rings within each chain are all nearly perfectly coplanar while the silver atoms are protruding toward the center of the double chains. Figure 4d shows a side view of a double chain highlighting the electrostatic Ag–O–Ag–O “quadrangle”. One oxygen atom of each triflate ion, O(1), has a short contact to a silver atom, Ag(1), within its associated chain (2.468(3) Å) and a just slightly longer contact to a silver atom Ag(1*) in the neighboring chain (2.627(3) Å). Similar Ag–oxyanion dimers have been observed previously in cyclic dicyanodiphenylacetylene

complexes of Ag(I) (15). A double-chain structure featuring alternating π stacking and ionic interactions is also present in the one-dimensional solid [AgX(3,6-di(4-pyridyl)-1,2,4,5-tetrazine)(MeCN)] ($X = \text{BF}_4, \text{PF}_6$) (16). The possibility that the silver atoms in **2** are pushed toward the center of the double chains by steric repulsions from the phenyl rings of the adjacent double chains can be dismissed on the basis of the relatively long Ag–C(arene) distances, ranging from 3.83–4.08 Å. The local distortions of the linear CN–Ag–CN chains also reveal a marked difference in the structural robustness of the isocyanide–silver and nitrile–silver linkages. As the Ag atom is “pulled out” from the ideally linear N–C–Ag–N–C grouping, the isocyanide carbon atom “follows” more than the nitrile nitrogen atom, causing the metal–isocyanide group Ag(1)–C(1)–N(1) to bend by only 8° while the metal–nitrile group Ag(1)–N(2)–C(2) bends by 20°. This result provides another indication that metal–nitrile bonds are probably not reliable linkages in situations where structural robustness is desired. We have previously observed the “collapse” of a normally linear Cu–N–C copper–nitrile angle to only 108° under the influence of crystal packing forces (4a, 4c).

From a general perspective, cyanoisocyanoarenes may be viewed as expanded neutral analogues of cyanide. In analogy to the coordination chemistry of cyanide (17), they can be expected to give rise to a potentially rich variety of coordination polymers. In this sense, the linear coordination polymer **2** is an expanded analogue of silver(I) cyanide, whose solid-state structure consists of linear–Ag–C–N–Ag–chains (18). In the context of this analogy, the structure of **2** may also be compared with the structure of AgCN·2AgNO₃ (19). The structure of this mixed salt features linear–Ag–C–N–Ag–chains separated by interspersed AgNO₃ units, whereby the oxygen atoms of the nitrate ions form relatively short contacts (3.0–3.2 Å) with the silver atoms in the neutral AgCN chains.

ACKNOWLEDGMENTS

Support for this work by the Committee on Conference and Research Grants of The University of Hong Kong and by the Hong Kong Research Grants Council is gratefully acknowledged.

REFERENCES

1. J. C. Bailar, in “Prep. Inorg. Reactions” (W. L. Jolly, Ed.), Vol. 1, pp. 1–25. Interscience, New York, 1964.

2. (a) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.* **20**, 1 (1976); (b) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins, and J. Liu, in “Supramolecular Architecture” (T. Bein, Ed.), ACS Symposium Series 499, Am. Chem. Soc., Washington, DC, 1992; (c) O. M. Yaghi, H. L. Li, Davis, D. Richardson, and T. L. Groy, *Acc. Chem. Res.* **31**, 474 (1998); (d) P. J. Hagrman, D. Hagrman, and J. Zubieta, *Angew. Chem., Int. Ed.* **38**, 2638 (1999).
3. (a) F. A. Cotton and Y. Kim, *J. Am. Chem. Soc.* **115**, 8511 (1993); (b) R. E. Melendez, C. V. K. Sharma, M. J. Zaworotko, C. Bauer, and R. D. Rogers, *Angew. Chem., Int. Ed. Engl.* **35**, 2213 (1996); (c) B. F. Abraham, S. R. Batten, H. Hamit, B. F. Hoskins, and R. Robson, *Angew. Chem., Int. Ed. Engl.* **34**, 820 (1996); (d) G. L. Ning, M. Munakata, L. P. Wu, M. Maekawa, T. Kuroda-Sowa, Y. Suenaga, and K. Sugimoto, *Inorg. Chem.* **38**, 1376 (1999).
4. (a) L.-F. Mao and A. Mayr, *Inorg. Chem.* **35**, 3183 (1996); (b) J. Guo and A. Mayr, *Inorg. Chim. Acta* **261**, 141 (1997); (c) A. Mayr and L.-F. Mao, *Inorg. Chem.* **37**, 5776 (1998); (d) A. Mayr and J. Guo, *Inorg. Chem.* **38**, 921 (1999); (e) K. Y. Lau, A. Mayr, and K.-K. Cheung, *Inorg. Chim. Acta* **285**, 223 (1999).
5. W. P. Fehlhammer and M. Fritz, *Chem. Rev.* **93**, 1243 (1993).
6. (a) L. Malatesta and F. Bonati, “Isocyanide Complexes of Transition Metals.” Wiley, New York, 1969; (b) E. Singleton and H. E. Oosthuizen, *Adv. Organomet. Chem.* **22**, 209 (1983).
7. D. Fortin, M. Drouin, M. Turcotte, and P. D. Harvey, *J. Am. Chem. Soc.* **119**, 531 (1997).
8. (a) D. Venkataraman, G. B. Gardner, S. Lee, and J. S. Moore, *J. Am. Chem. Soc.* **117**, 11600 (1995); (b) G. B. Gardner, Y.-H. Kiang, S. Lee, A. Asgaonkar, and D. Venkataraman, *J. Am. Chem. Soc.* **118**, 6946 (1996); (c) W. Choe, Y.-H. Kiang, Z. Xu, and S. Lee, *Chem. Mater.* **11**, 1776 (1999).
9. Z.-L. Lu, A. Mayr, and K.-K. Cheung, *Inorg. Chim. Acta* **284** (1999) 205.
10. DENZO, in “The HKL Manual—A description of programs DENZO, XDISP, and SCALEPACK,” written by D. Gewirth, with the cooperation of the program authors Z. Otwinowski and W. Minor, 1995.
11. TeXsan: Crystal Structure Analysis Package, Molecular Structure Corp., 1985 & 1992.
12. (a) M. E. Squires and A. Mayr, *Inorg. Chim. Acta* **264**, 161 (1997); (b) S. Wang, A. Mayr, and K.-K. Cheung, *J. Mater. Chem.* **8**, 1561 (1998); (c) L. Yang, K.-K. Cheung, and A. Mayr, *J. Organomet. Chem.* **585**, 26 (1999).
13. “Gmelins Handbuch der Anorganischen Chemie,” Silber, Teil B1, p. 291. Verlag Chemie, Weinheim, 1971.
14. H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.* **80**, 507 (1958).
15. K. A. Hirsch, S. R. Wilson, and J. S. Moore, *J. Am. Chem. Soc.* **119**, 10401 (1997).
16. M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, and M. Schröder, *Angew. Chem., Int. Ed.* **36**, 2327 (1997).
17. K. R. Dunbar and R. A. Heintz, *Prog. Inorg. Chem.* **45**, 283 (1997).
18. (a) C. D. West, *Z. Kristallogr.* **90**, 555 (1935); (b) “Gmelins Handbuch der Anorganischen Chemie,” Silber, Teil B3, p. 299. Verlag Chemie, Weinheim, 1973.
19. D. Britton and J. D. Dunitz, *Acta Crystallogr.* **19**, 815 (1965).