

Bimetallic Coordination Polymers via Combination of Substitution-Inert Building Blocks and Labile Connectors

Malgorzata Kondracka and Ulli Englert*

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany

Received April 25, 2008

A rational approach to the synthesis of silver–chromium mixed-metal coordination polymers is presented: 3-cyanoacetylacetonate (HacacCN) features two potential binding sites. After deprotonation, it has been used as a chelating didonate ligand in the pseudo octahedral complex $\text{Cr}(\text{acacCN})_3$; two polymorphs of this compound have been identified. In its protonated form, HacacCN was employed as a N donor toward $\text{Ag}(\text{I})$. Both functionalities may be exploited within the same solid: The chromium complex and silver salts of weakly coordinating anions have been successfully combined to mixed-metal coordination polymers. $\text{Cr}(\text{acacCN})_3$ plays the role of a substitution-inert tecton with predictable bonding geometry which interacts with the conformationally soft silver cations via two or all three of its peripheral nitrile groups. From an equimolar amount of both constituents, six solids featuring a 1:1 ratio between Cr- and Ag-derived building blocks were obtained in good yield; their structures depend on the counteranions and the cocrystallized solvent and correspond either to 2D networks with (6,3) or augmented (4,4) topology or, in one case, adopt a 3D connectivity. In addition, three products with a Cr/Ag = 2:1 stoichiometry have been isolated: they adopt two-dimensional network structures.

Introduction

The synthesis of coordination polymers with novel structures and potentially useful properties attracts considerable interest.^{1,2} The resulting metal-organic frameworks display a variety of architectures³ and fascinating dynamic behavior.⁴ A popular strategy for the synthesis of coordination polymers involves the reaction of polydentate bridging ligands (“spacers”) and metal ions and relies on the self-assembly of these basic components.^{2,5} Systems involving more than one kind of metal may in principle be accessible by the same method,

albeit formation of simpler products can compete and the success rate may drop with increasing complexity. An obvious modular alternative consists of the synthesis of suitable intermediate coordination compounds of one metal in a first step, followed by cross-linking with the help of a second metal. Under the condition that the intermediate is sufficiently inert with respect to ligand substitution, the latter approach can result in extended structures not accessible via a simple one-pot reaction. Domasevitch et al. have successfully applied this stepwise strategy to the synthesis of mixed-metal coordination polymers incorporating main group metal derivatives and transition metal cations.^{6,7} We were interested in coordination polymers involving two different transition metals in an ordered fashion. Obviously, the inertness of at least one of the components favors a modular synthesis and helps to avoid byproduct, for example, due to transmetalation.

* Author to whom correspondence should be addressed. E-mail: ullrich.englert@ac.rwth-aachen.de.

- (1) (a) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330. (b) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466–1496. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Porta, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 317–322. (d) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511–522.
- (2) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658.
- (3) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.
- (4) (a) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737–2738. (b) Hu, C.; Englert, U. *Angew. Chem., Int. Ed.* **2005**, *44*, 2281–2283. (c) Hu, C.; Englert, U. *Angew. Chem., Int. Ed.* **2006**, *45*, 3457–3459. (d) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O’Keeffe, M.; Yaghi, O. M. *Science* **2008**, *319*, 939–943.

- (5) (a) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022–2043. (b) Ouahab, L. *Chem. Mater.* **1997**, *9*, 1909–1926, and references therein. (d) Braga, D. *J. Chem. Soc., Dalton Trans.* **2000**, 3705–3713. (e) Ohba, M.; Okawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313–328.
- (6) Vreshch, V. D.; Chernega, A. N.; Howard, J. A. K.; Sieler, J.; Domasevitch, K. V. *Dalton Trans.* **2003**, 1707–1711.
- (7) Vreshch, V. D.; Lysenko, A. B.; Chernega, A. N.; Howard, J. A. K.; Krautscheid, H.; Sieler, J.; Domasevitch, K. V. *Dalton Trans.* **2004**, 2899–2903.

Braunstein and co-workers have reported a chain polymer based on an alternating sequence of square-planar Pt(II) and Ag(I) cations.⁸ In our approach, a classical substitution-inert coordination complex of trivalent chromium with pendant potential donor sites in the periphery was combined with silver salts of weakly or noncoordinating anions. We have deliberately chosen the ligand 3-cyanopentane-2,4-dionate (acacCN), in view of the well-established inertness of chromium(III)acetylacetonates⁹ on the one hand and the moderate donor capabilities¹⁰ of the nitrile group on the other. In this contribution, we communicate the structures of the building blocks, their successful aggregation via weaker bonds to flexible Ag(I) centers, and the crystal structures of a series of bimetallic networks. Burrows and co-workers have recently published mixed-metal coordination compounds based on similar building blocks, namely, 3-cyanoacetylacetonates of Cu(II), Fe(III), and Al(III) and silver nitrate.¹¹

Experimental Section

A. Materials and Methods. All chemicals purchased were of reagent grade or better and were used without further purification. HacacCN was prepared according to the method of Belot et al.¹² IR spectra were recorded on a Nicolet Avatar 360 E.S.P. spectrometer in nujol between KBr windows. Microanalyses were performed with a Heraeus CHNO-Rapid apparatus. Complexes **4a**, **4b**, and **5a** represent rather instable solvates which, however, lose a well-defined fraction of the solvent of crystallization when dried under a vacuum: In these cases, the composition for which the analytical data have been obtained differs from the composition of a rapidly cooled single crystal, and the diverging formula for the bulk solid has been explicitly listed together with the microanalytical results.

B. Syntheses. a. Cr(acacCN)₃, 1. This compound has been synthesized according to the procedure described for Cr(acac)₃.¹³ A total of 0.53 g of CrCl₃·6H₂O (2 mmol) was dissolved in 50 mL of water. A total of 0.50 g (8 mmol) of urea and 0.82 g (6.6 mmol) of HacacCN were added to this solution. The resulting mixture was covered with a watch glass and heated to 90 °C for 16 h. The green solution turned violet, and after about 2 h, violet needles formed. The crystals were filtered and dried in vacuo. The crude product was purified by recrystallization from hot toluene upon the addition of hot petroleum ether. Yield: 0.33 g (0.77 mmol, 39%). IR (cm⁻¹): 2206 (m), 1598 (s), 1021 (m), 933 (m), 708(m), 632(m), 549 (m), 462 (m). Anal. calcd for C₁₈H₁₈CrN₃O₆: C, 50.95; H, 4.27; N, 9.90. Found: C, 50.46; H, 3.93; N, 9.54. Crystals for X-ray diffraction studies of two different polymorphs were obtained from solutions in toluene–methanol (**α-1**) and toluene (**β-1**) by slow evaporation at room temperature.

b. [Ag(HacacCN)₂]CF₃SO₃, 2. AgCF₃SO₃ (0.128 g, 0.5 mmol) was dissolved in toluene (5 mL). To this solution was added 0.125

g (1 mmol) of HacacCN in toluene (5 mL) in a single portion. Stirring was continued for 30 min, and the clear solution was cooled to 4 °C and left to stand undisturbed. After 24 h, colorless platelike crystals of **2** appeared, which were filtered and dried under a vacuum. Yield: 0.15 g (60%). The product is stable for at least 6 months when kept at 4 °C in the dark. IR (cm⁻¹): 2239 (s), 1580 (m), 1222 (m), 926 (m), 632 (m), 516 (m). Decomp. 140 °C. Anal. calcd for C₁₃H₁₄N₂O₇AgSF₃: C, 30.78; H, 2.78; N, 5.52. Found: C, 30.13; H, 3.20; N, 5.38.

Bimetallic Coordination Polymers with a Cr/Ag = 1:1 Ratio. [Cr(acacCN)₃Ag]CF₃SO₃·0.5C₆H₅Me·MeOH, 3a, and [Cr(acacCN)₃Ag]CF₃SO₃·0.5C₆H₆·MeOH, 3b. To a solution of Cr(acacCN)₃ (0.043 g, 0.1 mmol) in benzene (5 mL) was added a solution of AgCF₃SO₃ (0.026 g, 0.1 mmol) in methanol/toluene (2 mL/2 mL). This mixture was heated up to 40 °C in order to dissolve precipitating Cr(acacCN)₃. The resulting clear solution was cooled down to room temperature and stored overnight at 4 °C. After this time, violet crystals of [Cr(acacCN)₃Ag]CF₃SO₃·0.5C₆H₅Me·MeOH, **3a**, appeared. Yield: 0.03 g (81%). The product is thermally stable up to 240 °C and stable for at least 6 months when kept at 4 °C in the dark. The analogous reaction conducted in methanol/benzene led to the formation of [Cr(acacCN)₃Ag]CF₃SO₃·0.5C₆H₆·MeOH, **3b**. IR (cm⁻¹): 2229(m), 1581(s), 935(m), 637(m). Anal. calcd for C₂₃H₂₅N₃O₁₀SF₃AgCr: C, 36.71; H, 3.35; N, 5.58. Found: C, 36.75; H, 3.55; N, 5.59.

d. [Cr(acacCN)₃Ag]PF₆·3MeOH, 4a. To a solution of Cr(acacCN)₃ (0.043 g, 0.1 mmol) in toluene (5 mL) was added a solution of AgPF₆ (0.024 g, 0.1 mmol) in methanol (5 mL). This reaction mixture was vigorously stirred for 10 min. The resulting clear solution was stored overnight at 4 °C. Violet platelike crystals of [Cr(acacCN)₃Ag]PF₆·3MeOH precipitated after 12 h. Crystals of **4a** desolvate and visibly decompose in the air within 15 min but are stable for at least 6 months in the mother liquor. The compound is thermally stable up to 180 °C. Yield: 0.04 g (55%). IR (cm⁻¹): 2236(s), 1588(s), 1075(s), 843(w), 460(w). Anal. calcd for [Cr(acacCN)₃Ag]PF₆·MeOH, C₁₉H₂₂N₃O₇PF₆CrAg: C, 32.17; H, 3.13; N, 5.92. Found: C, 33.45; H, 3.27; N, 6.05.

e. [Cr(acacCN)₃Ag]PF₆·4C₆H₆, 4b. To a solution of Cr(acacCN)₃ (0.043 g, 0.1 mmol) in benzene (5 mL) was added a solution of AgPF₆ (0.024 g, 0.1 mmol) in methanol (5 mL). This reaction mixture was vigorously stirred for 10 min. The resulting clear solution was stored overnight at 4 °C. Violet platelike crystals of [Cr(acacCN)₃Ag]PF₆·4C₆H₆ precipitated after 12 h. Crystals of **4b** desolvate and visibly decompose in the air within 15 min but are stable for at least 6 months in the mother liquor. Upon desolvation, two of the four equivalents of benzene per formula unit evaporate. The compound is thermally stable up to 110 °C. Yield: 0.05 g (60%). IR (cm⁻¹): 2242(s), 1582(s), 1169(w), 936(w), 837(m), 688(w), 637(w), 557(m), 460(w). Anal. calcd for [Cr(acacCN)₃-Ag]PF₆·2C₆H₆, C₃₀H₃₀N₃O₆PF₆CrAg: C, 43.23; H, 3.63; N, 5.04. Found: C, 42.26; H, 3.64; N, 5.80.

f. [Cr(acacCN)₃Ag]BF₄·2MeOH·0.5C₆H₅Me, 5a. A solution of AgBF₄ (0.020 g, 0.1 mmol) in methanol (5 mL) was added to a solution of Cr(acacCN)₃ (0.043 g, 0.1 mmol) in toluene (7 mL) under vigorous stirring at 40 °C, and this reaction temperature was maintained for an additional 5 min. The resulting clear solution was cooled down to room temperature and stored overnight at 4 °C. After this time, violet, bricklike crystals of composition [Cr(acacCN)₃Ag]BF₄·2MeOH·0.5C₆H₅Me were obtained. Dry crystals lose the incorporated solvent within several hours. The product decomposes at 195 °C to give a black powder. Yield: 0.047 g (62%). IR (cm⁻¹): 2219(s), 1597(m), 1215(m), 1073(w), 841(m),

(8) Margraf, G.; Pattacini, R.; Messaoudi, A.; Braunstein, P. *Chem. Commun.* **2006**, 3098–3100.

(9) Saito, K. *Pure Appl. Chem.* **1974**, *38*, 325–340.

(10) Jacob, V.; Mann, S.; Huttner, G.; Walter, O.; Zsolnai, L.; Kaifer, E.; Rutsch, P.; Kircher, P.; Bill, E. *Eur. J. Inorg. Chem.* **2001**, 2625–2640.

(11) Burrows, A. D.; Cassar, K.; Mahon, M. F.; Warren, J. E. *Dalton Trans.* **2007**, 2499–2509.

(12) Silvernail, C. M.; Yap, G.; Sommer, R. D.; Rheingold, A. L.; Day, V. W.; Belot, J. A. *Polyhedron* **2001**, *20*, 3113–3117.

(13) Fernelius, W. C.; Blanch, J. E. *Inorg. Synth.* **1957**, *5*, 130.

Table 1. Crystal Data for Cr(acacCN)₃, **α-1** and **β-1**, and [Ag(HacacCN)₃]CF₃SO₃, **2**

| | α-1 | β-1 | 2 |
|---|---|---|--|
| formula | C ₁₈ H ₁₈ CrN ₃ O ₆ | C ₁₈ H ₁₈ CrN ₃ O ₆ | C ₁₃ H ₁₄ AgF ₃ N ₂ O ₇ S |
| fw (g mol ⁻¹) | 424.35 | 424.35 | 507.19 |
| cryst syst | monoclinic | trigonal | monoclinic |
| space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 3̄ <i>c</i> 1 | <i>Pn</i> |
| <i>a</i> (Å) | 15.177(3) | 10.5565(4) | 5.6312(7) |
| <i>b</i> (Å) | 12.993(9) | | 6.9583(8) |
| <i>c</i> (Å) | 20.862(4) | 10.2081(9) | 22.768(3) |
| <i>β</i> (deg) | 108.435(3) | | 90.024(2) |
| <i>V</i> (Å ³) | 3902.6(12) | 985.18(10) | 892.13(19) |
| <i>Z</i> | 8 | 2 | 2 |
| <i>T</i> (K) | 130(2) | 130(2) | 130(2) |
| <i>D</i> _{calcd} (g cm ⁻³) | 1.444 | 1.431 | 1.888 |
| <i>μ</i> (Mo Kα) (mm ⁻¹) | 0.626 | 0.620 | 1.316 |
| measd/ind reflns | 39448/9720 | 15357/990 | 13346/5080 |
| <i>R</i> _{int} | 0.0603 | 0.0434 | 0.0229 |
| wR2 | 0.1246 | 0.1536 | 0.0799 |
| <i>R</i> 1 | 0.0775 | 0.0587 | 0.0306 |
| GOF on <i>F</i> ² | 1.032 | 1.131 | 1.059 |

680(w), 466(m). Anal. calcd for [Cr(acacCN)₃Ag]BF₄·0.5MeOH, C₃₇H₄₀Ag₂B₂Cr₂F₈N₆O₁₃ (**5a-3MeOH-C₇H₈**): C, 34.99; H, 3.17; N, 6.61. Found: C, 34.70; H, 3.49; N, 6.749.

g. [Cr(acacCN)₃Ag]BF₄·MeOH·1.5C₆H₆, **5b**. A solution of AgBF₄ (0.020 g, 0.1 mmol) in methanol (5 mL) was added to a solution of Cr(acacCN)₃ (0.043 g, 0.1 mmol) in benzene (6 mL) under vigorous stirring at a temperature of 40 °C. This reaction mixture was heated to 40 °C for an additional 5 min. The resulting clear solution was cooled down to room temperature and stored overnight at 4 °C. After this time, violet, bricklike crystals of [Cr(acacCN)₃Ag]BF₄·MeOH·1.5C₆H₆, **5b**, were obtained. The product decomposes at 185 °C to give a black powder. Yield: 0.034 g (53%). IR (cm⁻¹): 2224(s), 1583(m), 1210(m), 1063(w), 934(m), 684(w), 666(m), 460 (w). Anal. calcd for C₅₅H₅₈Ag₂B₂Cr₂F₈N₆O₁₃: C, 43.91; H, 3.88; N, 5.59. Found: C, 43.46; H, 3.82; N, 5.72.

Bimetallic Coordination Polymers with a Cr/Ag = 2:1 Ratio.

h. {[Cr(acacCN)₃]₂Ag}PF₆·MeOH, **6**. A solution of AgPF₆ (0.012 g, 0.05 mmol) in methanol (8 mL) was added to a solution of Cr(acacCN)₃ (0.043 g, 0.1 mmol) in benzene (6 mL) under vigorous stirring at room temperature. This reaction mixture was heated up to 35 °C to dissolve precipitating Cr(acacCN)₃. The resulting clear solution was cooled down to room temperature and stored overnight at 4 °C. After this time, violet, brickshaped crystals of {[Cr(acacCN)₃]₂Ag}PF₆·MeOH, **6**, formed in up to 49% yield (0.055 g). In several preparations, **6** was obtained together with the corresponding mixed-metal coordination polymer with a Cr/Ag = 1:1 ratio, that is, [Cr(acacCN)₃Ag]PF₆·4C₆H₆, **4b**. Crystals of **6** disintegrate due to solvent loss within 1 h under ambient conditions. The compound rapidly decomposes at 220 °C. IR (cm⁻¹): 2229(s), 1581(s), 935(s), 637(w). Anal. calcd for C₃₇H₄₀N₆O₁₃PF₆Cr₂Ag: C, 39.20; H, 3.56; N, 7.41. Found: C, 38.73; H, 3.45; N, 7.28.

i. {[Cr(acacCN)₃]₂Ag}BF₄·C₆H₅Me, **7a**. A solution of AgBF₄ (0.010 g, 0.05 mmol) in methanol (4 mL) was added to a solution of Cr(acacCN)₃ (0.043 g, 0.1 mmol) in toluene (8 mL) under vigorous stirring at room temperature. The resulting clear solution was cooled down to room temperature and stored overnight at 4 °C. After this time, a few violet crystals of {[Cr(acacCN)₃]₂Ag}BF₄·C₆H₅Me, **7a**, were obtained. This compound was only obtained as a byproduct together with an unidentified microcrystalline solid. The IR spectrum and microanalytical data of the bulk material are not in agreement with the composition of **7a** derived from single-crystal X-ray diffraction and are therefore not reported. Crystals of **7a** decompose at 190 °C, giving a black powder.

j. {[Cr(acacCN)₃]₂Ag}BF₄·MeOH, **7b**. A solution of AgBF₄ (0.010 g, 0.05 mmol) in methanol (6 mL) was added to a solution

Table 2. Crystal Data for [Cr(acacCN)₃Ag]CF₃SO₃·0.5C₆H₅Me·MeOH, **3a**; [Cr(acac)₃Ag]CF₃SO₃·0.5C₆H₆·MeOH, **3b**; and [Cr(acacCN)₃Ag]PF₆·3MeOH, **4a**

| | 3a | 3b | 4a |
|---|--|---|--|
| formula | C ₄₇ H ₅₂ Ag ₂ Cr ₂ F ₆ N ₆ O ₂₀ S ₂ | C ₂₃ H ₂₅ AgCrF ₃ N ₃ O ₁₀ S | C ₂₁ H ₃₀ AgCrF ₆ N ₃ O ₉ P |
| fw (g mol ⁻¹) | 1518.81 | 752.39 | 773.32 |
| cryst syst | triclinic | triclinic | triclinic |
| space group | <i>P</i> 1̄ | <i>P</i> 1̄ | <i>P</i> 1̄ |
| <i>a</i> (Å) | 10.5781(7) | 10.5635(10) | 11.3280(12) |
| <i>b</i> (Å) | 12.4976(8) | 12.3559(12) | 12.3001(13) |
| <i>c</i> (Å) | 13.5413(9) | 13.5021(13) | 13.210(2) |
| <i>α</i> (deg) | 115.5540(10) | 115.4480(10) | 109.693(2) |
| <i>β</i> (deg) | 107.1900(10) | 107.4980(10) | 105.948(2) |
| <i>γ</i> (deg) | 94.0830(10) | 92.5230(10) | 105.465(2) |
| <i>V</i> (Å ³) | 1501.35(17) | 1486.7(2) | 1529.5(3) |
| <i>Z</i> | 1 | 2 | 2 |
| <i>T</i> (K) | 130(2) | 110(2) | 130(2) |
| <i>D</i> _{calcd} (g cm ⁻³) | 1.673 | 1.681 | 1.679 |
| <i>μ</i> (Mo Kα) (mm ⁻¹) | 1.158 | 1.169 | 1.134 |
| measd/ind reflns | 32203/8590 | 22483/8544 | 33337/8419 |
| <i>R</i> _{int} | 0.0357 | 0.0281 | 0.0332 |
| wR2 | 0.0765 | 0.0751 | 0.1436 |
| <i>R</i> 1 | 0.0390 | 0.0326 | 0.0686 |
| GOF on <i>F</i> ² | 1.021 | 1.031 | 1.027 |

of Cr(acacCN)₃ (0.043 g, 0.1 mmol) in benzene (8 mL) under vigorous stirring at room temperature. This reaction mixture was heated up to 40 °C to dissolve precipitating Cr(acacCN)₃. The resulting clear solution was stored overnight at 4 °C. After this time, violet, brick-shaped crystals of **7b** were obtained. After 12 h, violet, brick-shaped crystals of {[Cr(acac)₃]₂Ag}BF₄·MeOH were obtained, together with the related compound **5b**. Disintegration of **7b** due to solvent loss occurs within 1 h under ambient conditions and much more rapidly at 200 °C, giving a black powder. In solution, the compound is stable for at least 6 months. Yield: 0.037 g (68%). IR (cm⁻¹): 2231(s), 1581(s), 934(m), 675(w), 464(m).

C. Crystallographic Studies. Intensity data for all structures were collected with a Bruker SMART APEX CCD detector on a D8 goniometer (Mo Kα radiation, λ = 0.71073 Å, graphite monochromator). Absorption corrections based on multiscan methods were applied.^{14,15} The structures were solved by direct methods¹⁶ and refined on *F*².¹⁷ Hydrogen atoms were included as riding in idealized positions. Calculations concerning space-filling properties and voids were performed with PLATON.¹⁵ For disordered structures, packing coefficients are less well-defined; in these cases, only one of the mutually exclusive sets of atom sites was taken into account. Crystal data, details on data collection, and convergence results for the structures **α-1**, **β-1**, and **2** are compiled in Table 1; those for the mixed-metal coordination polymers with in a Cr/Ag = 1:1 stoichiometry, **3a–5b**, in are in Tables 2 and 3, and those for compounds **6–7b** (with a Cr/Ag = 2:1 ratio) are in Table 4. We have been able to crystallize **1** reproducibly in the form of two polymorphs, **α-1** (from toluene/methanol = 1:1) and **β-1** (from pure toluene); powder diffraction (cf. Supporting Information) on the bulk samples confirmed that pure phases were obtained. Crystals of **2** are characterized by a monoclinic angle very close to 90° and represent twins by lattice merohedry¹⁸ in space group *Pn*. The structure is pseudosymmetric with respect to a mirror plane: A

(14) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

(15) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

(16) Sheldrick, G. M. *SHELXS97*; University of Göttingen: Göttingen, Germany, 1997.

(17) Sheldrick, G. M. *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

(18) Nespolo, M.; Ferraris, G. Z. *Kristallogr.* **2000**, *215*, 77–81.

Table 3. Crystal Data for [Cr(acacCN)₃Ag]PF₆·4C₆H₆, **4b**; [Cr(acacCN)₃Ag]BF₄·2MeOH·0.5C₆H₅Me, **5a**; and [Cr(acacCN)₃Ag]BF₄·MeOH·1.5C₆H₆, **5b**

| | 4b | 5a | 5b |
|---|--|--|--|
| formula | C ₄₂ H ₄₂ AgCrF ₆ N ₃ O ₆ P | C ₄₇ H ₆₀ Ag ₂ B ₂ Cr ₂ F ₈ N ₆ O ₁₆ | C ₅₅ H ₅₈ Ag ₂ B ₂ Cr ₂ F ₈ N ₆ O ₁₃ |
| fw (g mol ⁻¹) | 989.63 | 1458.37 | 1504.43 |
| cryst. syst. | monoclinic | triclinic | monoclinic |
| space group | <i>P2₁/c</i> | <i>P1</i> | <i>C2/c</i> |
| <i>a</i> (Å) | 11.8269(10) | 11.1960(9) | 21.5012(10) |
| <i>b</i> (Å) | 20.0536(18) | 11.9875(9) | 11.7251(6) |
| <i>c</i> (Å) | 18.5766(16) | 13.5929(11) | 25.7606(11) |
| α (deg) | | 110.429(2) | |
| β (deg) | 100.4860(10) | 104.050(2) | 103.492(2) |
| γ (deg) | | 105.843(2) | |
| <i>V</i> (Å ³) | 4332.3(7) | 1524.6(2) | 6315.1(5) |
| <i>Z</i> | 4 | 1 | 4 |
| <i>T</i> (K) | 130(2) | 130(2) | 100(2) |
| <i>D</i> _{calcd} (g cm ⁻³) | 1.517 | 1.588 | 1.582 |
| μ (Mo K α) (mm ⁻¹) | 0.815 | 1.070 | 1.033 |
| measd/ind reflns | 64913/12890 | 27479/12668 | 74021/15183 |
| <i>R</i> _{int} | 0.0508 | 0.0401 | 0.0970 |
| wR2 | 0.0757 | 0.1216 | 0.1564 |
| R1 | 0.0666 | 0.0706 | 0.0914 |
| GOF on <i>F</i> ² | 1.045 | 1.049 | 1.085 |

Table 4. Crystal Data for {[Cr(acacCN)₃]₂Ag}PF₆·MeOH, **6**; {[Cr(acacCN)₃]₂Ag}BF₄·C₆H₅Me, **7a**; and {[Cr(acacCN)₃]₂Ag}BF₄·MeOH, **7b**

| | 6 | 7a | 7b |
|---|---|--|--|
| formula | C ₃₇ H ₄₀ AgCr ₂ F ₆ N ₆ O ₁₃ P | C ₄₃ H ₄₄ AgBCr ₂ F ₄ N ₆ O ₁₂ | C ₃₇ H ₄₀ AgBCr ₂ F ₄ N ₆ O ₁₃ |
| fw (g mol ⁻¹) | 1133.59 | 1135.52 | 1075.43 |
| cryst. syst. | monoclinic | monoclinic | monoclinic |
| space group | <i>P2₁/c</i> | <i>P2₁/c</i> | <i>P2₁/c</i> |
| <i>a</i> (Å) | 8.0245(6) | 10.1929(10) | 7.8367(5) |
| <i>b</i> (Å) | 23.9405(18) | 15.2910(15) | 24.3686(17) |
| <i>c</i> (Å) | 23.5600(18) | 31.306(3) | 23.2360(16) |
| β (deg) | 98.8690(10) | 94.308(2) | 96.3383(16) |
| <i>V</i> (Å ³) | 4472.0(6) | 4865.6(8) | 4410.2(5) |
| <i>Z</i> | 4 | 4 | 4 |
| <i>T</i> (K) | 110(2) | 130(2) | 110(2) |
| <i>D</i> _{calcd} (g cm ⁻³) | 1.684 | 1.550 | 1.620 |
| μ (Mo K α) (mm ⁻¹) | 1.040 | 0.918 | 1.009 |
| measd/ind reflns | 66778/13232 | 70645/13501 | 52591/9058 |
| <i>R</i> _{int} | 0.0516 | 0.0602 | 0.1148 |
| wR2 | 0.1121 | 0.1360 | 0.1359 |
| R1 | 0.0580 | 0.0708 | 0.1038 |
| GOF on <i>F</i> ² | 1.068 | 1.085 | 1.006 |

relevant fraction of the final electron density (84%) matches the symmetry of the supergroup *Pmn2₁*, but a tentative refinement in this orthorhombic space group resulted in an extensively disordered structure model. The hydroxyl H atoms in the neutral HacacCN moieties of **2** were detected as local electron density maxima close to the oxygen atoms with longer C–O separations; their coordinates were idealized (O–H = 0.84 Å). In the case of compound **3**, two isotopic solvates containing both one molecule of methanol and 0.5 molecules of arene per formula unit, **3a** and **3b**, were obtained; the toluene molecule in the former is disordered with respect to a crystallographic inversion center. Complex **5a** crystallizes in the noncentrosymmetric space group *P1*; the space group is in agreement with the intensity statistics observed, and tentative transformation to the centrosymmetric supergroup did not result in a satisfactory structure model. The crystal used for intensity data collection was an inversion twin. In compound **5b**, a benzene molecule and one of the BF₄⁻ anions show orientational disorder, and the second tetrafluoroborate anion is disordered over two

general positions, both close to a crystallographic center of inversion. In **7a**, the toluene molecule is disordered with respect to an inversion center. Internal agreement factors, convergence results, and resolution indicate that the crystal quality for single crystals of **7b** is lower than that of the remaining compounds. Crystallographic data for all structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications, nos. CCDC-682971 (for **α-1**) through -682982 (for **7b**).

Results

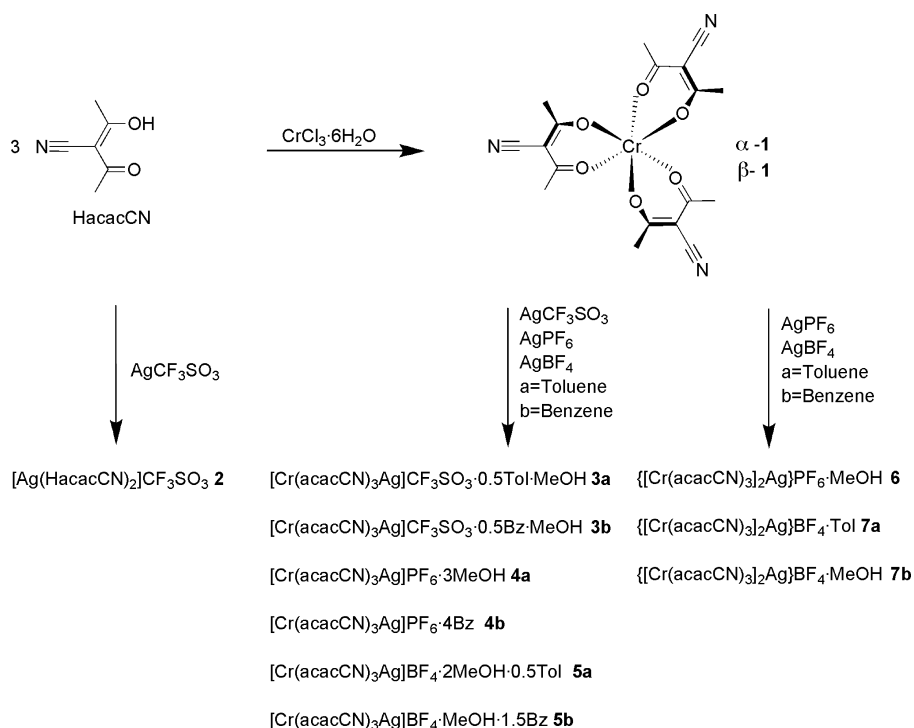
Scheme 1 provides an overview of the synthetic pathway and all products characterized in the context of this work.

Our strategy for the synthesis of bimetallic coordination polymers proved to be successful. The role of the substitution-inert building block was reliably taken over by **1**, and we will shortly describe this complex which, in terms of crystal engineering, may be addressed as a synthon¹⁹ or, in view of its predictable peripheric donor sites pointing to the vertices of an equilateral triangle, as a tecton.²⁰ Compound **1** adopts the expected pseudo-octahedral CrL₃ geometry with three chelating β-diketonato ligands. In its crystals, **1** shows dimorphism: The combination of powder and single-crystal X-ray diffraction shows that the two polymorphs **α-1** and **β-1** can be obtained reproducibly as phase pure solids. Complex **α-1** crystallizes in the monoclinic space group *P2₁/n*; the unit cell contains two independent molecules in a general position which differ in conformation: the dihedral angles between best planes through the acac ligands range from 73.60(9) to 87.10(9) for one and from 81.21(9) to 89.81(9) for the second molecule. Complex **α-1** is structurally related and most probably isomorphous to the Fe(acacCN)₃ described recently.¹¹ The second phase, **β-1**, is trigonal, space group *P3c1*, with the molecule showing the highest possible site symmetry, *D*₃, compatible with the point group of the molecule. Space filling is slightly more efficient for the monoclinic phase with two independent molecules; packing coefficients amount to 0.686 for **α-1** and 0.678 for **β-1**.

Obviously, the peripheric N atoms of the nitrile groups in CrL₃ are decisive for the formation of extended structures along the line of our mixed-metal network synthesis. For reasons of symmetry, these donors subtend N⋯Cr⋯N angles of exactly 120° in **β-1**. For the two symmetrically independent molecules in the α phase, however, these angles vary between 106.78(4) and 144.28(4)° and suggest a certain flexibility for **1** as a two-connected linker or three-connected node. Figure 1 shows a displacement ellipsoid plot of a molecule in **β-1**.

In the IR spectrum of complex **1**, a band of medium intensity appears at 2206 cm⁻¹; it can be assigned to the stretching vibration of the cyano groups. The intense absorptions in the region 1650–1500 cm⁻¹ may be attributed to the conjugated C=C–C=O region; for a metal-coordinated β-dionato moiety, this absorption is observed at higher wave numbers, for example, at 1598 cm⁻¹ in the case of **1**, whereas the corresponding absorption for the uncoordinated

(19) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *21*, 2311–2327.
(20) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696–4698.

Scheme 1. Synthesis and Composition of the Building Block, **1**; Chain Polymer, **2**; and the Bimetallic Polymeric Solids, **3a–7b**

ligand HacacCN is observed at 1538 cm^{-1} . Table 5 compiles the wavenumbers associated with the above-mentioned vibrations for the ligand HacacCN, its derivatives **1** and **2**, and all mixed metal coordination polymers reported in this work. This synopsis of IR spectra leads to the conclusion that coordination of the terminal nitrogen in the cyano group results in a moderate, reliably detectable shift in wave numbers. Compounds **6** and **7b** show both coordinating and free nitrile groups; the latter cause a shoulder at the low wavenumber side of the IR absorption associated with the CN stretching vibration.

We envisaged that the ligand acacCN^- should exhibit only moderate donor properties. Upon coordination, it

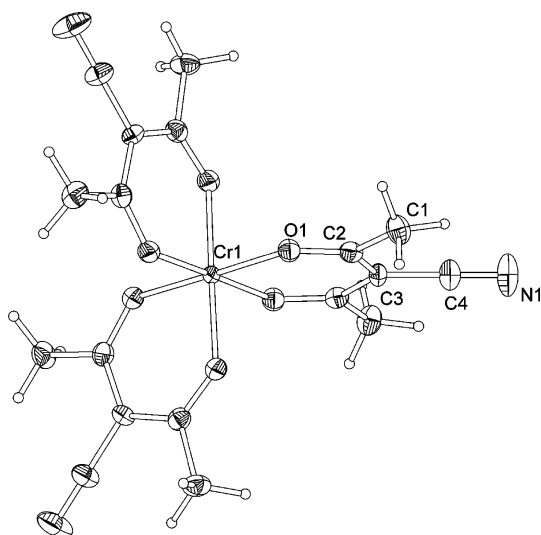


Figure 1. Displacement ellipsoid plot of a molecule in β -**1**. Ellipsoids are drawn at 50% probability; H atoms are shown with arbitrary radii. Selected interatomic distances [Å]: [range for α -**1** in square brackets]: Cr1–O1, 1.952(2) [1.9450(18)–1.9591(17)]; C4–N1, 1.144(5) [1.142(4)–1.153(4)].

should allow for a variety of rather soft geometries around the labile Ag(I) linkers. The question whether HacacCN or its deprotonated anion may act as ligands for metal coordination is not rhetoric: This moiety does not simply represent a nitrile but also features electron-withdrawing groups in the neighborhood of the potential donor site. Attempts to obtain bimetallic products from reactions of complex **1** with several Zn(II) salts rather gave mixtures of the components. The formation of **2** from silver triflate and HacacCN in toluene may therefore be regarded as a proof of principle: The neutral compound HacacCN does not bind to Ag(I) as shown in Figure 2. Each silver cation is coordinated by two cyano groups of HacacCN ligands and a triflate oxygen atom; the latter moiety bridges neighboring Ag centers and generates a 1D polymer.

In compound **2**, the neutral ligand HacacCN binds via its nitrile group, whereas the potentially chelating O,O donor sites do not participate in metal coordination. Only a few compounds have been structurally characterized in which the cyano group of the HacacCN ligand is responsible for bonding.²²

Mixed-Metal Coordination Polymers. Coordination of the nitrile group in the free HacacCN has been achieved in

Table 5. Selected IR Data

| compound | $\nu \text{ (cm}^{-1}\text{)}$ | |
|--|--------------------------------|------|
| | C=C–C=O | CN |
| HacacCN | 1538 | 2218 |
| $\text{Cr}(\text{acacCN})_3$, 1 | 1598 | 2206 |
| $[\text{Ag}(\text{HacacCN})_2]\text{CF}_3\text{SO}_3$, 2 | 1580 | 2239 |
| $[\text{Cr}(\text{acacCN})_3\text{Ag}]\text{CF}_3\text{SO}_3 \cdot 0.5\text{C}_6\text{H}_5\text{Me} \cdot \text{MeOH}$, 3a | 1581 | 2229 |
| $[\text{Cr}(\text{acacCN})_3\text{Ag}]\text{PF}_6 \cdot 3\text{MeOH}$, 4a | 1588 | 2236 |
| $[\text{Cr}(\text{acacCN})_3\text{Ag}]\text{PF}_6 \cdot 4\text{C}_6\text{H}_6$, 4b | 1582 | 2242 |
| $[\text{Cr}(\text{acacCN})_3\text{Ag}]\text{BF}_4 \cdot 2\text{MeOH} \cdot 0.5\text{C}_6\text{H}_5\text{Me}$, 5a | 1597 | 2219 |
| $[\text{Cr}(\text{acacCN})_3\text{Ag}]\text{BF}_4 \cdot \text{MeOH} \cdot 1.5\text{C}_6\text{H}_6$, 5b | 1583 | 2224 |
| $\{\{\text{Cr}(\text{acacCN})_3\}_2\text{Ag}\}\text{PF}_6 \cdot \text{MeOH}$, 6 | 1581 | 2229 |
| $\{\{\text{Cr}(\text{acacCN})_3\}_2\text{Ag}\}\text{BF}_4 \cdot \text{MeOH}$, 7b | 1581 | 2231 |

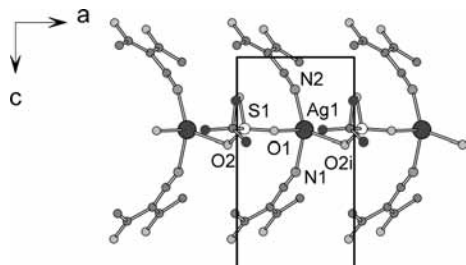


Figure 2. Projection of an infinite chain in **2**.²¹ Relevant interatomic distances [Å]: Ag1–N1, 2.234(8); Ag1–N2, 2.229(5); Ag1–O1, 2.447(3); Ag1–O2ⁱ, 2.348(4); $i = x + 1, y, z$.

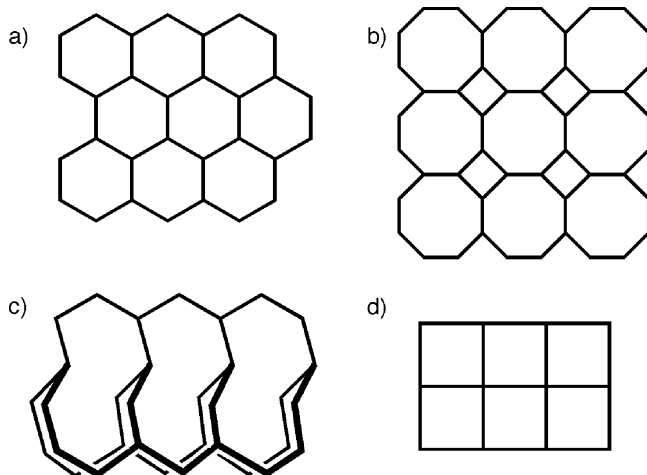


Figure 3. Schematic representation of the network topologies encountered. (a) (6,3), (b) $t\{4,4\}$, (c) (10,3), (d) (4,4) net.

2. Starting from substitution-inert complex **1**, rather than from its free ligand HacacCN and from silver salts of weakly or noncoordinating anions, we set out to synthesize mixed-metal networks, namely, cationic coordination polymers with alternating chromium and silver centers. The resulting solids may be classified with respect to composition and topology. The former approach has been followed in Scheme 1: **3a–5b** can be prepared as phase-pure products in good yields; the ratio between the building blocks (Cr tectons versus Ag(I) linkers) in the solids matches the 1:1 reaction stoichiometry. From preparations conducted in a Cr/Ag = 2:1 stoichiometry, single crystals of **6–7b** have been isolated. These solids are obtained, however, concomitant with the corresponding 1:1 products (e.g., **6** with **4b**) or even as byproducts only, see the Experimental Section. In the mixed-metal polymers, the compound numbers can be associated with the counteranions: Compounds **3** are triflates, **4** and **6** are hexafluorophosphates, and compounds **5** and **7** are tetrafluoroborates. In most cases, reactions in toluene and benzene resulted in different solids denoted as **a** and **b**, respectively.

Which topologies will our products adopt? Under the condition that each peripheric nitrile moiety in the CrL₃ tecton **1** binds to a silver cation and that the equimolar reaction stoichiometry is reflected in a Cr/Ag = 1:1 ratio in the coordination polymers, the formation of ($n,3$) nets can be expected: Among these, the (6,3) net (Figure 3a) represents a particularly popular, and the most regular, arrangement. In

contrast to the more rigid geometry of the three-connected node **1**, the coordination around the Ag(I) cation is less predictable: It may involve additional coordination to anions or solvent molecules in variable geometries and is not only compatible with the above-mentioned honeycomb structure but also with less obvious answers such as the truncated (4,4) (Figure 3b) or the three-dimensional (10,3) net (Figure 3c). An additional alternative arises if the composition of the coordination polymer follows a Cr/Ag = 2:1 stoichiometry and only two of the –CN donor groups of the CrL₃ tecton bind to Ag(I) cations. In this case, the latter may perform as four-connected nodes linked by bidentate **1**, and a (4,4) net may result, as depicted in Figure 3d.

We will first consider the structures of the 1:1 coordination polymers. Complexes **3a**, **3b**, **4a**, and **5a** are related; they all crystallize in the triclinic system with similar lattice parameters. These compounds form two-dimensional networks and share the same topology. A closer inspection suggests treating them as two pairs, namely, the isomorphous solids **3a** and **3b** on the one hand and the group/subgroup related **4a/5a** on the other hand.

In **3a** and **3b**, the asymmetric unit contains one Cr(acacCN)₃ tecton, one Ag(I) cation, one counteranion, and a small number of atoms associated with the incorporated solvent of crystallization. The structures are isomorphous; as **3a** shows disorder with respect to the toluene solvent molecule, only **3b** is documented in Figure 4. Table 6 compiles the most relevant interatomic distances and angles for both structures.

The coordination of the silver cations in **3a** and **3b** is distorted trigonal-pyramidal with three Ag–N bonds in the plane and a fourth axial vertex occupied by the triflate anion which binds to silver via an oxygen atom. The Ag(I) coordination in **3b** and the other types of mixed-metal networks discussed in this work are compared in Figure 5.

The supramolecular structures of the bimetallic networks **3a** and **3b** intuitively match the disposition of the peripheral cyano groups within the CrL₃ tecton **1**. Together with the trigonal-planar coordination of the silver cations, the formation of a dense mixed-metal hexagonal structure is not surprising, and a regular 2D topology, namely, an almost undistorted (6,3) net, originates from the combination of CrL₃ triangles with the trigonal-planar coordinated Ag atom. The stacking of these layers follows the sequence (AB)(AB)…, with coordinated cations and solvent molecules intercalated between layers A and B (Figure 4b) and, hence, leads to the formation of a bilayer system. The interlayer distance within (AB) amounts to 5.78 and that between two (AB) bilayers to 3.79 Å.

Complexes **4a** and **5a** also correspond to (6,3) nets with respect to their 2D structures. They are closely related with respect to the disposition of the metal cations in the unit cells. Complex **4a** crystallizes in the triclinic space group $P\bar{1}$, whereas **5a** belongs to the noncentrosymmetric subgroup $P1$. Figure 6 shows a 2D layer (a) and the layer stacking (b,c) in both structures.

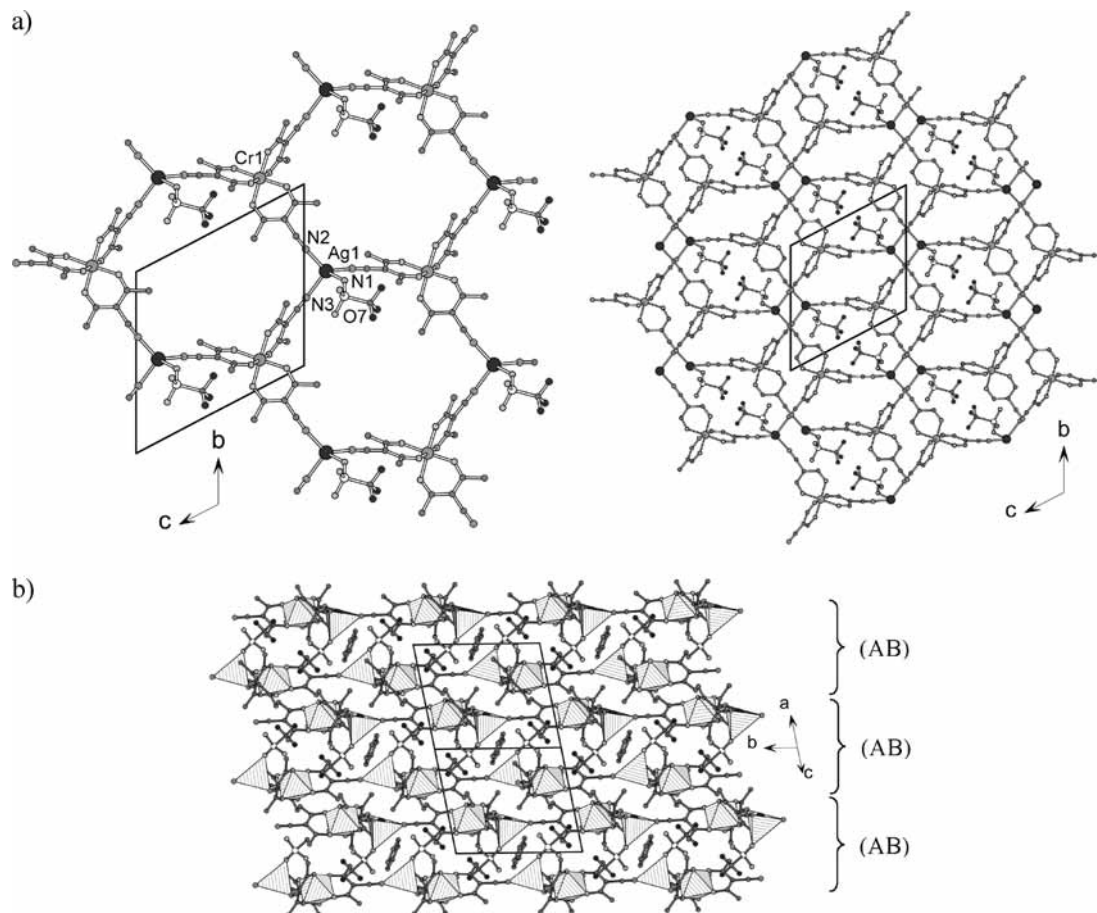


Figure 4. (a) Cr/Ag heterobimetallic hexagons in the structure of compound **3b**. Compound **3a** is isomorphous. (b) Two-dimensional network of **3b**, viewed along the [101] direction. The polyhedra represent $\{\text{CrO}_6\}$ octahedra and $\{\text{AgN}_3\text{O}\}$ tetrahedra. Hydrogen atoms have been omitted for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for Compounds **3a** and **3b**

| [Ag(acacCN) ₃]CF ₃ SO ₃ ·0.5C ₆ H ₅ Me·MeOH, 3a | | | | | |
|--|------------|-----------------|-----------|------------------|-----------|
| Ag(1)–N(1) | 2.1763(18) | N(1)–Ag(1)–N(2) | 129.99(7) | N(1)–Ag(1)–O(7) | 95.51(7) |
| Ag(1)–N(2) | 2.2216(17) | N(1)–Ag(1)–N(3) | 122.82(7) | N(2)–Ag(1)–O(7) | 102.45(7) |
| Ag(1)–N(3) | 2.2479(18) | N(2)–Ag(1)–N(3) | 101.97(7) | N(3)–Ag(1)–O(7) | 94.52(7) |
| Ag(1)–O(7) | 2.5377(17) | | | | |
| [Cr(acacCN) ₃ Ag]CF ₃ SO ₃ ·0.5C ₆ H ₆ ·MeOH, 3b | | | | | |
| Ag(1)–N(1) | 2.187(3) | N(1)–Ag(1)–N(2) | 133.06(8) | N(1)–Ag(19)–O(7) | 96.50(10) |
| Ag(1)–N(2) | 2.230(2) | N(1)–Ag(1)–N(3) | 121.89(7) | N(2)–Ag(1)–O(7) | 98.91(10) |
| Ag(1)–N(3) | 2.262(2) | N(2)–Ag(1)–N(3) | 100.30(8) | N(3)–Ag(1)–O(7) | 95.74(7) |
| Ag(1)–O(7) | 2.537(2) | | | | |

Both an additional common feature and the main difference between the structures of **4a** and **5a** concern the environment of the Ag(I) cations. The diagrams of the coordination environment in Figure 5d and e show the presence of relatively short $\text{Ag}\cdots\text{Ag}$ distances of ca. 3.1 Å in both solids. These so-called argentophilic²³ interactions do not increase the dimensionality of the solids but rather result in the formation of bilayer systems in which the silver cations of one layer are superimposable with those of the adjacent. The distances between adjacent bilayers are quite similar and amount to 6.26 Å in **4a** and to 6.11 Å in **5a**. However, the intermetal contacts involve cations related by crystallographic inversion in the case of **4a** (Figure 6b), whereas they occur between independent atoms in **5a** (Figure 6c). The neighborhood of these two metal atoms indeed differs in the latter compound,

with one methanol molecule and one tetrafluoroborate anion completing the trigonal-bipyramidal coordination of the Ag(I) cations. Selected interatomic distances and angles have been compiled in Table 7 for **4a** and Table 8 for **5a**.

Compound **4b**, albeit chemically similar to **4a**, adopts a different two-dimensional structure: The flexibility in the Ag(I) linkers does not only allow the formation of hexagonal layers as above. In **3a**, **3b**, **4a**, and **5a**, the coordination of the silver cation by three nitrile N atoms can be described as nearly regular with three similar N–Ag–N angles. The situation is quite different in **4b**, where the metal exhibits a strongly distorted tetra-coordination by three NC groups and one carbon from the solvent benzene ring; the N–Ag–N angles amount to 92.41(7), 108.16(8), and 131.38(7)°. The Ag(I) cations still play the role of three-connected vertices for a polymeric structure,

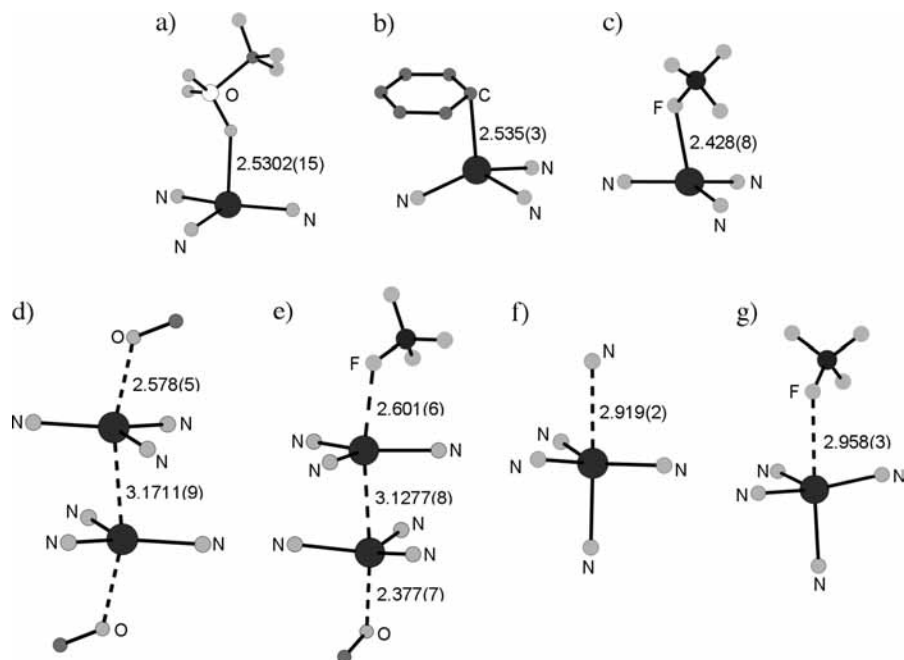


Figure 5. Representative coordination environments of the Ag(I) cations in (a) **3b**, (b) **4b**, (c) **5b**, (d) **4a**, (e) **5a**, (f) **6**, and (g) **7a**. Only the coordinating anions or solvent and nitrile N atoms are shown; distances are given in angstroms.

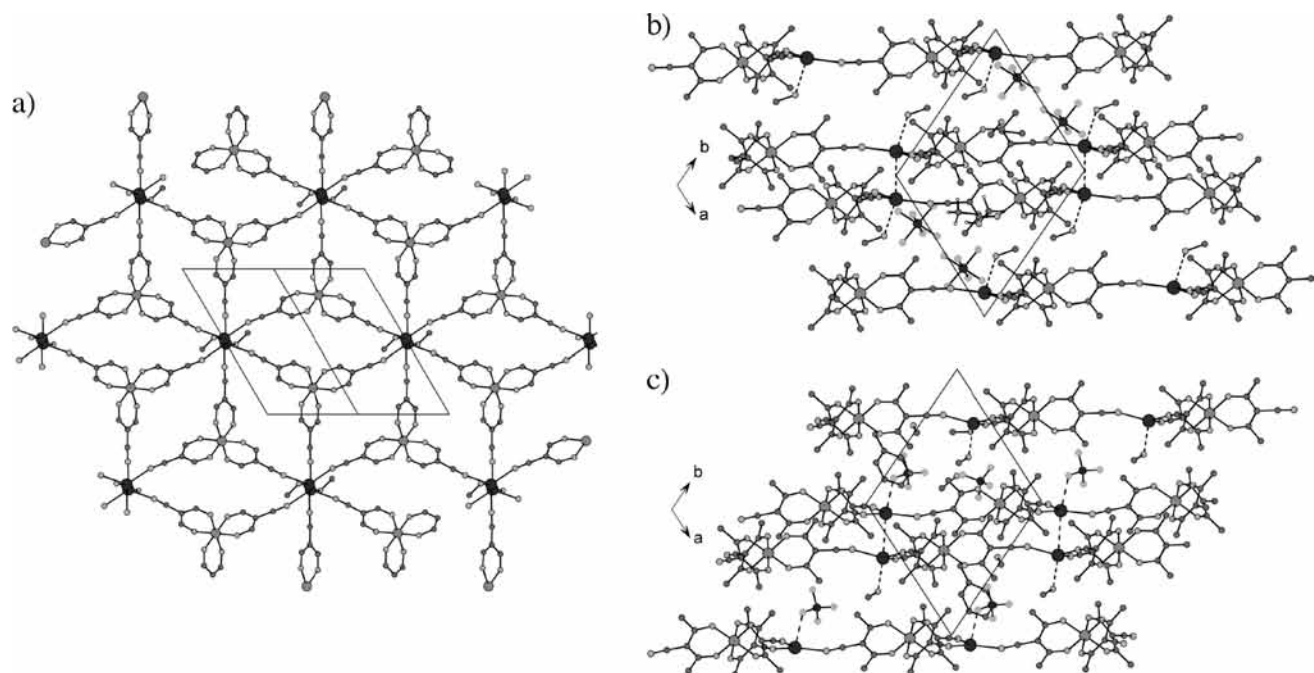


Figure 6. (a) Cr/Ag heterometallic hexagons in the structure of compound **4a** viewed along the [1-10] direction. (b) Bilayer system in the structure of compound **4a**. (c) Bilayer system in the structure of compound **5a**. For clarity, methyl groups in a and hydrogen atoms in a–c have been omitted.

Table 7. Selected Bond Distances (Å) and Angles (deg) for Compound **4a**

| [Cr(acacCN) ₃ Ag]PF ₆ ·3MeOH, 4a | | | | | |
|---|-----------|---|------------|--|------------|
| Ag(1)–N(1 ^a) | 2.163(3) | N(1 ^a)–Ag(1)–N(2) | 108.95(14) | N(3 ^b)–Ag(1)–O(7) | 99.22(17) |
| Ag(1)–N(2) | 2.201(3) | N(1 ^a)–Ag(1)–N(3 ^b) | 126.79(14) | N(1 ^a)–Ag(1)–Ag(1) | 86.29(11) |
| Ag(1)–N(3 ^b) | 2.271(4) | N(2)–Ag(1)–N(3 ^b) | 123.49(14) | N(2)–Ag(1)–Ag(1 ^c) | 75.92(10) |
| Ag(1)–O(7) | 2.578(5) | N(1 ^a)–Ag(1)–O(7) | 80.80(17) | N(3 ^b)–Ag(1)–Ag(1 ^c) | 97.34(10) |
| Ag(1)–Ag(1 ^c) | 3.1712(9) | N(2)–Ag(1)–O(7) | 97.84(16) | O(7)–Ag(1)–Ag(1 ^c) | 163.02(13) |

^a *x*, *y*, *z* + 1. ^b *x* + 1, *y* + 1, *z* + 1. ^c *−x*, *−y* + 2, *−z* + 1.

but the “collapsed triangles”⁷ with one angle close to 90° are particularly suitable for the generation of an arrangement that may be addressed as a truncated or augmented semiregular

network (cf. Figure 3b for a schematic representation). Figure 7 shows the structure of **4b**, and selected interatomic distances and angles are listed in Table 9.

Table 8. Selected Bond Distances (Å) and Angles (deg) for Compound **5a**

| [Cr(acacCN) ₃ Ag]BF ₄ ·2MeOH·0.5C ₆ H ₅ Me, 5a | | | | | |
|---|-----------|------------------|------------|-------------------|------------|
| Ag(1)–N(1) | 2.207(6) | N(1)–Ag(1)–N(2) | 112.7(3) | N(4)–Ag(2)–N(5) | 119.8(3) |
| Ag(1)–N(2) | 2.273(7) | N(1)–Ag(1)–N(3) | 132.5(2) | N(4)–Ag(2)–N(6) | 118.3(3) |
| Ag(1)–N(3) | 2.192(6) | N(2)–Ag(1)–N(3) | 114.7(2) | N(5)–Ag(2)–N(6) | 116.6(2) |
| Ag(1)–F(1) | 2.601(6) | N(1)–Ag(1)–F(1) | 88.6(3) | N(4)–Ag(2)–O(13) | 98.4(3) |
| Ag(1)–Ag(2) | 3.1277(8) | N(2)–Ag(1)–F(1) | 100.1(2) | N(5)–Ag(2)–O(13) | 95.6(3) |
| Ag(1)–N(4) | 2.212(7) | N(3)–Ag(1)–F(1) | 83.7(3) | N(6)–Ag(2)–O(13) | 99.2(3) |
| Ag(1)–N(5) | 2.230(6) | N(1)–Ag(1)–Ag(2) | 88.95(18) | N(4)–Ag(2)–Ag(1) | 85.8(2) |
| Ag(1)–N(6) | 2.225(6) | N(2)–Ag(1)–Ag(2) | 94.45(18) | N(5)–Ag(2)–Ag(1) | 78.73(18) |
| Ag(1)–O(13) | 2.377(7) | N(3)–Ag(1)–Ag(2) | 87.10(16) | N(6)–Ag(2)–Ag(1) | 82.31(19) |
| | | F(1)–Ag(1)–Ag(2) | 165.00(17) | O(13)–Ag(2)–Ag(1) | 174.13(19) |

The structure of **4b** incorporates eight-membered and trapezoid four-membered rings with alternating Ag and Cr vertices. The resulting coordination network occupies only 34.2% of the crystal volume (cf. Conclusions) and hence provides sufficiently large voids for hosting guest molecules. In the present case, not only the PF₆[−] anions but also four symmetrically independent benzene molecules are intercalated, which form a kind of solvent layer. [Cd{AlL₃}(CH₃OH)Br₂]·2CHCl₃·2CH₃OH adopts a more regular but topologically equivalent structure.⁷

In contrast to all other mixed-metal solids described in this work, the remaining compound with a Cr/Ag = 1:1 stoichiometry, **5b**, is associated with a three-dimensional rather than a two-dimensional network structure. The network topology of the compound corresponds to a (10,3)-b network. The (10,3)-b framework or ThSi₂-type net²⁴ can be associated with the Schläfli symbol 10³ and a vertex symbol 10₂.10₄.10₄. Figure 8 shows that **5b** features two interpenetrating 3D + 3D → 3D networks of this (10,3)-b type.

The individual nets are related by inversion and represent the IIa class.²⁵ The asymmetric unit contains one Ag(I) cation

in a general position. A first tetrafluoroborate is located on a 2-fold crystallographic axis; disorder in this moiety is limited to the peripheric fluorine atoms. For charge compensation, a second BF₄[−] anion of the same multiplicity is required; it resides in a general position between two Ag(I) cations with a Ag···Ag separation of 7.55 Å. In agreement with the dimensions for tetrafluoroborate,²⁶ this anion is disordered over two sites.

Compounds **6**, **7a**, and **7b** share a Cr/Ag = 2:1 stoichiometry. In contrast to the 1:1 mixed-metal networks, the Cr(acacCN)₃ building block does not act as a vertex but rather as a bidentate linker with one dangling nitrile function which remains either completely noncoordinating (compound **7a**, see below) or only interacts with a rather distant Ag(I) cation via a Ag···N contact longer than 2.9 Å, which is the case for compounds **6** and **7b**. Figure 9 shows that these compounds can be associated with a two-dimensional layer structure if only the much shorter Ag–N bonds are taken into account: Ag(I) then results as trigonal-pyramidal with three shorter Ag–N bonds of 2.238(5)–2.312(5) Å in equatorial positions and one longer bond of 2.393(8) Å in the apical position.

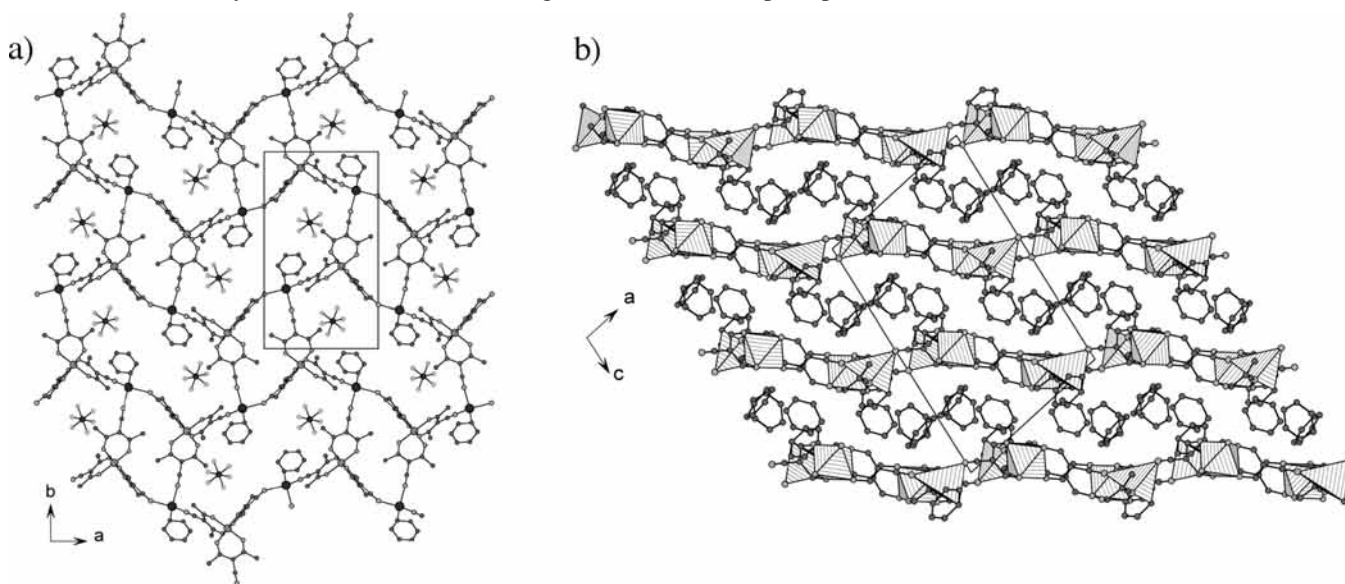


Figure 7. (a) Semiregular t{4,4} net of compound **4b**. (b) View parallel to the stacked layers in **4b**, showing the interstitial benzene molecules. The polyhedra represent {CrO₆} octahedra and {AgN₃C} tetrahedra. Hydrogen atoms and the acac methyl groups in b have been omitted for clarity.

Table 9. Selected Bond Distances (Å) and Angles (deg) for Compound **4b**

| [Cr(acacCN) ₃ Ag]PF ₆ ·4C ₆ H ₆ 4b | | | | | |
|---|------------|---|------------|--------------------------------|------------|
| Ag(1)–N(1 ^a) | 2.328(2) | N(1 ^a)–Ag(1)–N(2 ^b) | 92.41(7) | N(1 ^a)–Ag(1)–C(19) | 106.81(10) |
| Ag(1)–N(2 ^b) | 2.2901(19) | N(1 ^a)–Ag(1)–N(3) | 108.16(18) | N(2 ^b)–Ag(1)–C(19) | 97.24(10) |
| Ag(1)–N(3) | 2.1724(19) | N(2 ^b)–Ag(1)–N(3) | 131.38(7) | N(3)–Ag(1)–C(19) | 116.77(78) |
| Ag(1)–C(19) | 2.535(3) | | | | |

^a $-x + 1, -y + 1/2, z + 1/2$. ^b $x - 1, -y + 1/2, z - 1/2$.

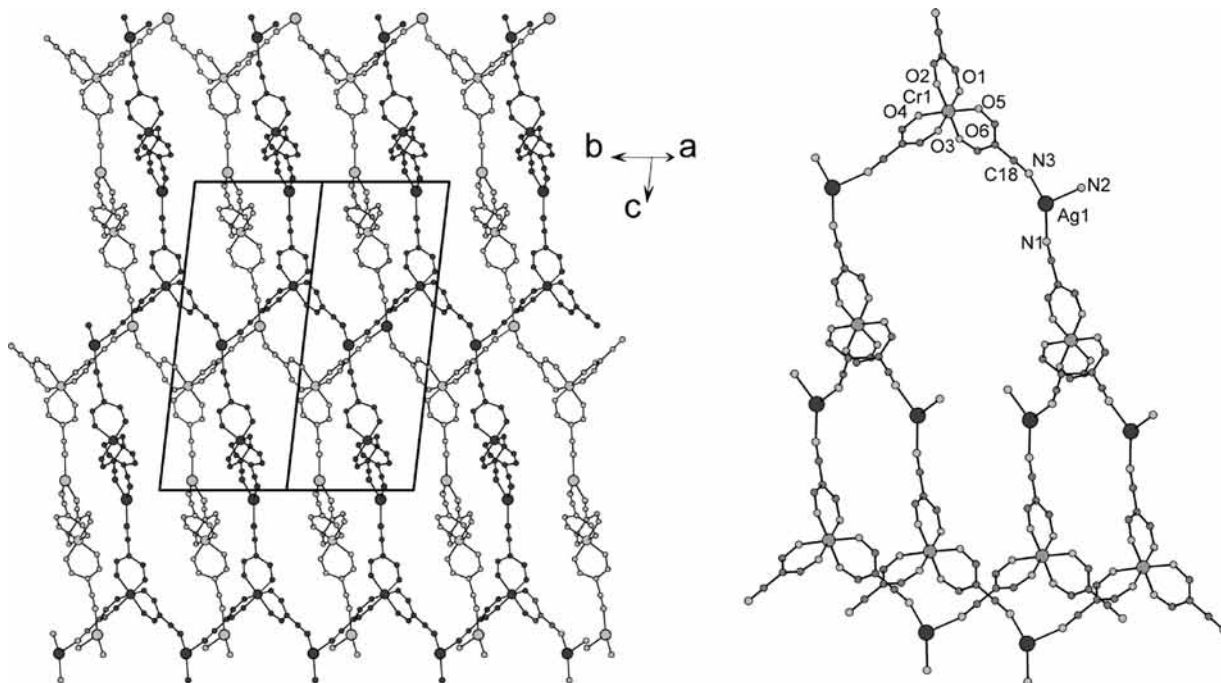


Figure 8. (a) Structure of compound **5b** showing two interpenetrating three-dimensional nets. (b) View of an adamantoid-like subunit in compound **5b**.

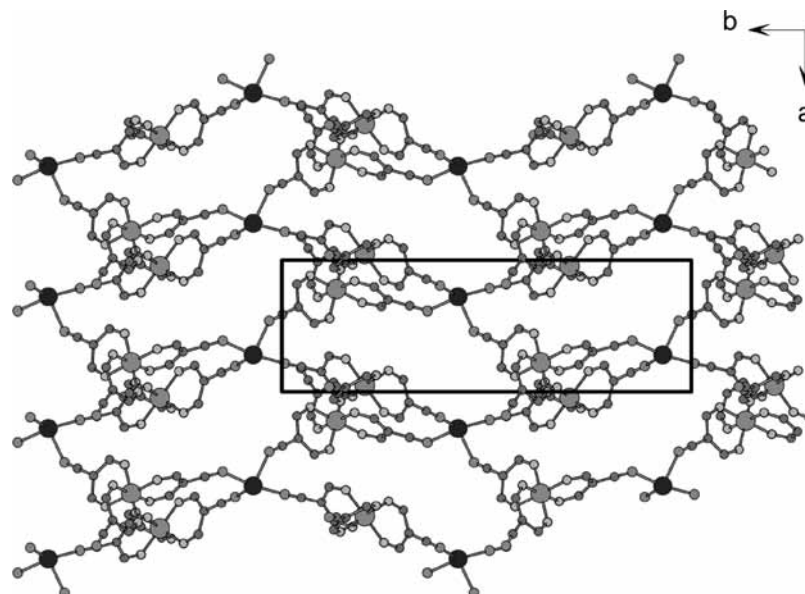


Figure 9. Cr/Ag heterobimetallic net of **6** with Ag(I) cations in trigonal-pyramidal (AgN_4) coordination. A distorted (4,4) net with Ag vertices and Cr linkers results.

The topologies of **6** and **7b** correspond to twisted 2D (4,4) nets. Interatomic distances and angles in **6** and **7b** are compiled in Table 10.

Figure 10 shows how the weakly interacting nitrile of each $\text{Cr}(\text{acacCN})_3$ linker is directed toward the adjacent layer in the [001] direction.

If this long $\text{Ag}(1)\cdots\text{N}(6)$ contact is considered a relevant connection, every second of the “free” *N*-cyano groups can be involved in the formation of a 3D network, and all nitrogen atoms but one (N5) are involved in coordinating or at least interacting with a silver cation. The new interaction in the third dimension is achieved by linking two different moieties, namely, three-connected Cr building blocks and five-connected Ag(I) cations. In

the overall network, each three-connected Cr vertex is linked to three four-connected Ag(I) vertices, and each five-connected Ag(I) vertex is connected to three three-connected CrL_3 tectons in two adjacent layers and to another two Cr building blocks which are only two-connected.

The structure of compound **7a** consists of corrugated (4,4) sheets, in which trigonal-pyramidal silver centers play the role of four-connected nodes and Cr complexes act as linkers (Figure 11a). Silver atoms within the sheet are nearly coplanar, whereas the linking Cr centers are located below and above, arranged in a way that the uncoordinated NC moieties are directed out of the sheet.

Table 10. Selected Bond Distances (Å) and Angles (deg) for Compounds **6** and **7b**

| [Cr(acac) ₃] ₂ Ag}PF ₆ ·MeOH, 6 | | | | | |
|--|----------|-------------------------------|-----------|---|------------|
| Ag(1)–N(1) | 2.405(3) | N(1)–Ag(1)–N(2 ^a) | 93.10(10) | N(2 ^a)–Ag(1)–N(3 ^b) | 103.45(9) |
| Ag(1)–N(2 ^a) | 2.271(2) | N(1)–Ag(1)–N(3 ^b) | 97.43(9) | N(2 ^a)–Ag(1)–N(4) | 140.08(8) |
| Ag(1)–N(3 ^b) | 2.349(2) | N(1 ^a)–Ag(1)–N(4) | 98.69(10) | N(3 ^b)–Ag(1)–N(4) | 112.52(9) |
| Ag(1)–N(4) | 2.238(2) | | | | |
| Ag(1)···N(6) | 2.911(6) | | | | |
| [Cr(acacCN) ₃] ₂ Ag}BF ₄ ·2C ₆ H ₅ Me, 7b | | | | | |
| Ag(1)–N(1) | 2.385(7) | N(1)–Ag(1)–N(2 ^a) | 98.2(3) | N(2 ^a)–Ag(1)–N(3 ^b) | 99.09(18) |
| Ag(1)–N(2 ^a) | 2.295(5) | N(1)–Ag(1)–N(3 ^b) | 100.5(2) | N(2 ^a)–Ag(1)–N(4) | 137.33(17) |
| Ag(1)–N(3 ^b) | 2.314(5) | N(1)–Ag(1)–N(4) | 91.7(2) | N(3 ^b)–Ag(1)–N(4) | 119.77(18) |
| Ag(1)–N(4) | 2.234(5) | | | | |

^a $-x, y + 1/2, -z + 1/2$. ^b $-x + 1, y + 1/2, -z + 1/2$.

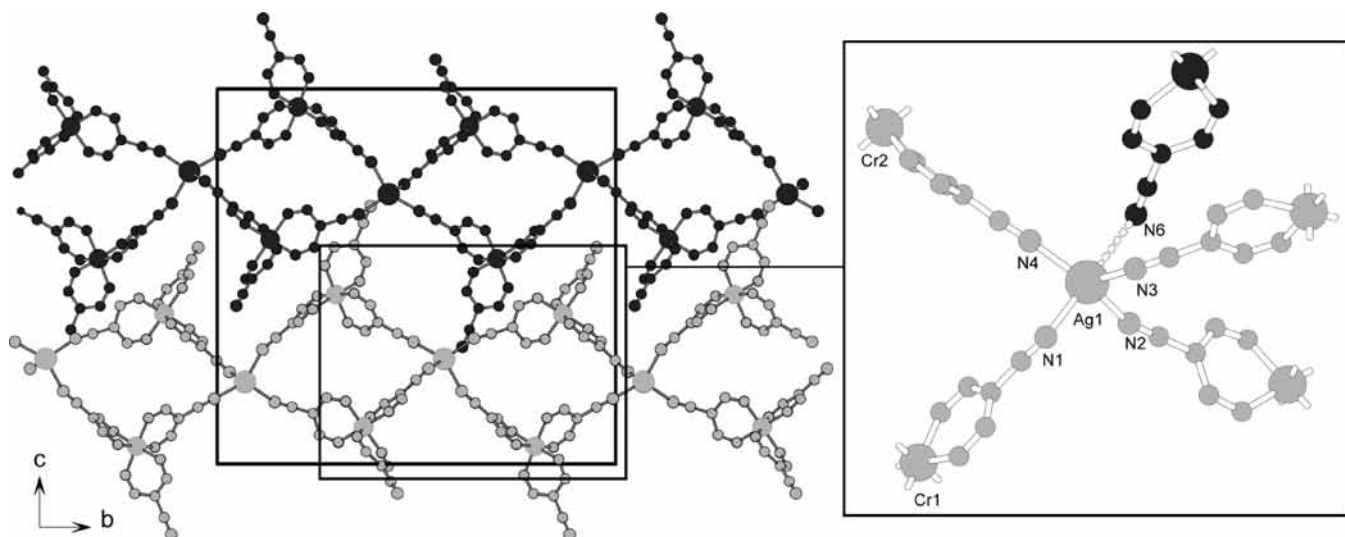


Figure 10. (a) 2D layers of **6** connected to each other by an additional weak coordination of nitrile groups to silver cations in the adjacent layer. (b) Coordination around the silver cation in **6**.

The corrugated nature of the sheets allows them to interpenetrate in pairs in a parallel fashion²⁷ and to form double layers. The individual sheets in the 2D + 2D → 2D network are related by translation along [100]; the structure of compound **7a** belongs to class I.²⁵ The noncoordinating dangling nitrile groups interdigitate with adjoining layers, as shown in Figure 11b. A rather weakly coordinated BF₄⁻ anion (Ag···F = 2.958(3)Å) is situated in channels which propagate along the crystallographic *b* axis (Figure 11b) and

which are delimited by the two corrugated sheets within each double layer. Selected interatomic distances and angles are listed in Table 11.

Conclusions

Our approach to combine the substitution-inert complex Cr(acacCN)₃ with Ag(I) as a linker allowed the formation of cationic bimetallic coordination polymers with alternating chromium and silver centers. After the discussion of the individual structures in the preceding section, we will shortly address the common features and trends encountered in these solids. The distance between neighboring Cr(III) and Ag(I) cations shows only modest variability, ranging from 7.5752(6) to 8.1926(9) Å for the 32 symmetrically independent observations. The soft coordination geometry around silver has already been highlighted in Figure 5: The cation may bind to three, four, or even five peripheric N atoms of Cr building blocks, and additional weak interactions with counteranions, solvent molecules, or neighboring silver cations can modify its geometry as connectors and, hence, the topology of the resulting structures. The broad distribution of Cr···N–Ag angles which can be almost linear but also smaller than 140° further contributes to the pronounced flexibility of the overall networks. As far as the cationic coordination polymers are concerned, their space filling is

- (21) Bergerhoff, G.; Brandenburg, K. *Diamond*; Visuelles Informationssystem für Kristallstrukturen: Bonn, Germany, 1996.
- (22) (a) Balahura, R. J.; Ferguson, G.; Johnston, A.; Ruhl, B. L. *Polyhedron* **1986**, *5*, 2075–2080. (b) Venetopoulou, D. K.; Keramidis, K. G.; Voutsas, G. P.; Rentzeperis, P. I.; Goubitz, K.; Tsiamis, C. Z. *Kristallogr.* **1994**, *209*, 170–174.
- (23) (a) Shorrocks, C. J.; Xue, B.-Y.; Kim, P. B.; Batchelor, R. J.; Patrick, B. O.; Leznoff, D. B. *Inorg. Chem.* **2002**, *41*, 6743–6753. (b) Chu, Q.; Swenson, D. C.; MacGillivray, L. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3569–3572. (c) Omary, M. A.; Webb, T. R.; Assefa, Z.; Shankle, G. E.; Patterson, H. H. *Inorg. Chem.* **1998**, *37*, 1380–1386. (d) Liu, X.; Guo, G.-C.; Fu, M.-L.; Liu, X.-H.; Wang, M.-S.; Huang, J.-S. *Inorg. Chem.* **2006**, *45*, 3679–3685. (e) Dobrzanska, L.; Raubenheimer, H. G.; Barbour, L. *Chem. Commun.* **2005**, 5050–5052. (f) Kalf, I.; Braun, M.; Wang, Y.; Englert, U. *CrystEngComm* **2006**, *8*, 916–922.
- (24) Oehrstroem, L.; Larsson, K. *Molecule-Based Materials: The Structural Network Approach*; Elsevier: Amsterdam, 2005; p 314.
- (25) Carlucci, L.; Ciani, G.; Proserpio, D. M. In *Making Crystals by Design*; Braga, D., Grepioni, F., Eds.; Wiley-VCH: Weinheim, Germany, 2007; p 58.
- (26) Rohl, A. L.; Mingos, D. M. P. *Inorg. Chim. Acta* **1993**, *212*, 5–13.
- (a) Mingos, D. M. P.; Rohl, A. L. *Dalton Trans.* **1991**, 3419–3425.

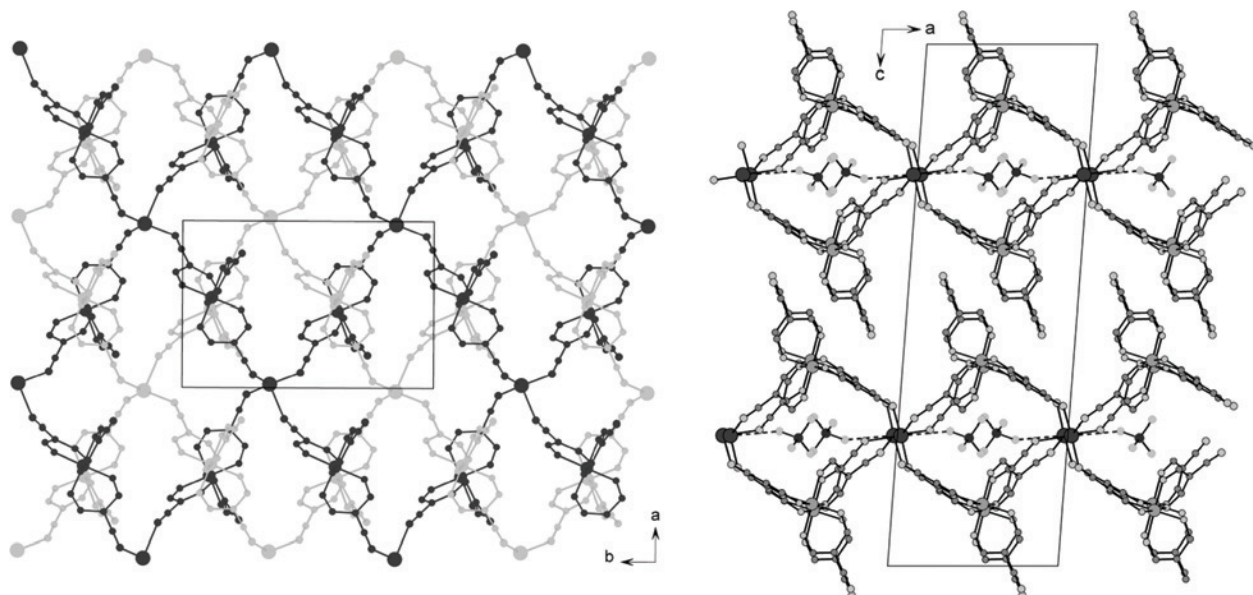


Figure 11. (a) Two interpenetrating (4,4) nets in compound **7a**. Terminal methyl groups, solvent molecules, and counteranions have been omitted. (b) Interdigitation of the peripheral nitrile groups from adjacent double layers in **7a**.

Table 11. Selected Bond Distances (Å) and Angles (deg) for Compound **7a**

| [[Cr(acacCN) ₃] ₂ Ag]BF ₄ ·2C ₆ H ₅ Me 7a | | | | | |
|--|----------|---|------------|-------------------------------|-----------|
| Ag(1)–N(1 ^a) | 2.226(3) | N(1 ^a)–Ag(1)–N(3) | 134.29(11) | N(1 ^a)–Ag(1)–F(1) | 80.83(10) |
| Ag(1)–N(3) | 2.261(3) | N(1 ^a)–Ag(1)–N(5) | 115.00(12) | N(3)–Ag(1)–F(1) | 71.53(8) |
| Ag(1)–N(5) | 2.293(3) | N(1 ^a)–Ag(1)–N(6 ^b) | 103.33(12) | N(5)–Ag(1)–F(1) | 95.28(10) |
| Ag(1)–N(6 ^b) | 2.358(3) | N(3)–Ag(1)–N(5) | 103.40(11) | N(6 ^b)–Ag(1)–F(1) | 162.60(9) |
| Ag(1)–F(1) | 2.958(3) | N(3)–Ag(1)–N(6 ^b) | 94.47(10) | | |
| | | N(5)–Ag(1)–N(6 ^b) | 98.08(12) | | |

^a $-x + 1, y + 1/2, -z + 1/2$. ^b $-x + 3, y - 1/2, -z + 1/2$.

rather low, and it is no surprise that all solids reported here incorporate additional solvent molecules. The overall space filling thus achieved ranges from 0.657 for compound **7a** to 0.714 for compound **6**. The CrL₃ tecton either induces 3-fold connectivity and a Cr/Ag = 1:1 network stoichiometry in compounds **3a–5b** or, alternatively, just serves as a linker with a dangling nitrile function with a Cr/Ag = 2:1 ratio in **6–7b**. In the former case, the packing coefficients for the polycationic network itself, that is, for the [CrL₃Ag]⁺ part of the structures, range from 0.478 to 0.505, whereas higher values between 0.574 and 0.630 are encountered for the latter {[CrL₃]₂Ag}⁺ type. Complex **4b**, the solid with the topology of a t{4,4} net and the eight-membered rings, represents an outlier with respect to these trends: Its network accounts for a space filling of 0.342 only, and crystals of the compound contain four molecules of benzene per bimetallic formula unit.

In retrospect, our solids merit a short comment with respect to the coordination ability of the “non-coordinating” anions. Several studies, most recently by Jung et al.,²⁸ have reported on numerous anion-exchange experiments in coordination solids and used their observation to establish a trend from strongly to weakly coordinating anions: NO₂[−] > NO₃[−] >

CF₃CO₂[−] > CF₃SO₃[−] > PF₆[−] > ClO₄[−] > BF₄[−]. However, the exchange experiments performed by Cohen et al.²⁹ show the ability of PF₆[−] and BF₄[−] anions to displace the triflate anion. At least with respect to the mixed-metal structures reported in this contribution, the PF₆[−] anion is less coordinating than BF₄[−]; the latter has been found interacting in **5a**, **5b**, and **7a**, whereas no example for coordination of hexafluorophosphate has been encountered.

Acknowledgment. The authors are grateful to Prof. J. Okuda for continuing support and to I. Kalf for help with the manuscript.

Note Added in Proof: A series of isomorphous structures studied by Chen and Mak (Chen, X.-D.; Mak, T. C. W. *Chem. Comm.* **2005**, 3529–3531) confirms our statement that the hexafluorophosphate anion represents the weakest potential coordination partner to silver.

Supporting Information Available: Crystallographic information for all structures in CIF format, displacement ellipsoid plots for all structurally characterized solids, and powder patterns for the two polymorphs of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC800748F

- (27) Batten, S. R.; Hoskins, B. F.; Robson, R. *Chem.–Eur. J.* **2000**, *6*, 156–161. (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494.
 (28) Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Park, K.-M.; Lee, S. S. *Inorg. Chem.* **2003**, *42*, 844–850. (a) Lee, J. W.; Kim, E. A.; Kim, Y. J.; Lee, Y.-A.; Pak, Y.; Jung, O.-S. *Inorg. Chem.* **2005**, *44*, 3151–3155.

- (29) Halper, S. R.; Do, L.; Stork, J. R.; Cohen, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 15255–15268.