New Ag(I) inorganic–organic coordination polymers and M(II) (M = Co(II) and Mn(II)) molecular complexes generated from a new type of fulvene ligand

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One new fulvene-type ligand **1** was synthesized successfully by aroylation reaction of substituted cyclopentadienyl anions. The coordination chemistry of fulvene ligands **1** and **2** were investigated. The study demonstrated that these fulvene-type ligands could be used as bidentate or chelating ligands to coordinate transition metal ions into coordination polymers or supramolecular complexes. Two novel one-dimensional Ag(I)–fulvene coordination polymers, namely [Ag(**1**)$_2$(PF$_6$)]·C$_6$H$_6$ and [Ag(**1**)$_2$(SbF$_6$)]·2C$_7$H$_8$, consisting of an Ag$_2$(ligand)$_2$ unit and two M(II) (M = Co(II) and Mn(II)) complexes, namely Co(**1**)$_2$·2C$_2$H$_5$OH and Mn(**2**)$_2$·2C$_2$H$_5$OH, with unusual seven-membered metallo-ring units were synthesized successfully. In the solid state, complexes **5** and **6** adopt a novel hydrogen-bonded one-dimensional chain motif.

Introduction

Within the field of inorganic–organic supramolecular chemistry, efforts to simultaneously utilize transition metal ions and organic spacers to form new extended framework structures through coordination or hydrogen-bonding interaction have yielded diverse new materials,[1–16] some of which have potential for applications such as catalysis, non-linear optics, gas separation, magnetic devices and molecular recognition.[17–23] In the long run, research performed today may well enable us in the future to actually predict the topology and/or the connectivity of crystalline lattices based on the molecular structures of the small building blocks used in their assembly. This will, ideally, lead to the rational design of framework materials for specific applications. Currently, the most efficient approach to prepare framework materials is *via* direct chemical combination of functional inorganic and organic components, a method which has proven quite fruitful.[1–16]

So far, various ligands, such as bipyridine-type and biphenyl-cyanide-type ligands, have been used for supramolecular building blocks,[1–3] however, to our knowledge, exploitation of the fulvene-type ligands have until recently remained unprecedented. It is well known that fulvene is one of the most important organic spacers in construction of organometallic complexes. On the other hand, free, active, polar organic functional groups in conjugated organic systems such as >C=O, –CR=N–, –COOH, –OH, are believed to play a central role in the construction of molecule-based functional materials.[24,25] Recently, we designed and synthesized a series of long, conjugated fulvene ligands with –CN and >C=O functional organic groups,[26] such as **1** and **2**, by the aroylation of substituted cyclopentadienyl anions, which were obtained from 6,6′-dialkylfulvene and phenyllithium (Scheme 1).[27] The structural versatility of these ligands is rich containing both carbonyl and cyano moieties. As we know, the cyano functional group on the aromatic ring is a good candidate for coordination bonding and has been exploited in the self-assembly of Ag-supramolecular architectures. Specifically, a series of very attractive Ag-coordination polymers based on 1,3,5-tris(4-cyanophenylethynyl)benzene,[28] 4,4′-biphenyldicarbonitrile,[29] 3,3′-dicyanodiphenylacetylene[30] and phenylacetylene nitriles
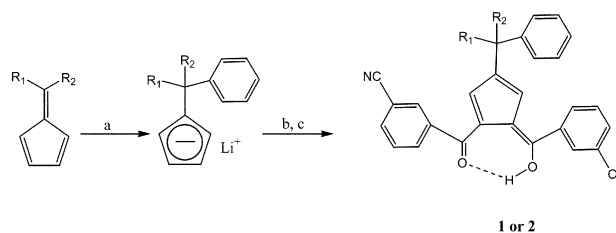
Scheme 1 Synthesis of compound **1**. Reagents and conditions: (a) PhLi, diethyl ether, 0 °C; (b) 3-cyanobenzoyl chloride, diethyl ether, 0 °C; (c) HCl (5%), room temperature.

with pendant oligo (ethylene oxide) side chains[31] has been reported by Moore and Lee. In addition, the 1,4-diketone structural unit in this type of ligands could be used as chelating groups to bind transition metals into seven-membered metallo-ring complexes which might be not achievable by other types of 1,4-diketone derivatives.

In this paper we demonstrate the successful use of these fulvene-type ligands **1** and **2** (Scheme 1) to link metal centers and to generate new coordination polymers, namely [Ag(**1**)$_2$(PF$_6$)]·C$_6$H$_6$ and [Ag(**2**)$_2$(SbF$_6$)]·2C$_7$H$_8$ and also molecular complexes, namely Co(**1**)$_2$·2C$_2$H$_5$OH and Mn(**2**)$_2$·2C$_2$H$_5$OH, with seven-membered metallo-ring units.

Experimental

Materials and methods

3-Cyanobenzoyl chloride and fulvene were prepared according to literature methods. The synthesis of **2** and its single crystal structure will be published elsewhere.[26b] AgPF$_6$, AgSbF$_6$, Co-(OAc)$_2$·2H$_2$O and Mn(OAc)$_2$·2H$_2$O (Acros) were used as obtained without further purification. Infrared (IR) samples

were prepared as KBr pellets, and spectra were obtained in the 400–4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. ^{1}H NMR data were collected using a JEOL FX 90Q NMR spectrometer. Chemical shifts are reported in δ relative to TMS. Elemental analyses were performed on a Perkin-Elmer Model 240C analyzer.

Synthesis of 1. A solution of 3-cyanobenzoyl chloride (1.70 g, 10.3 mmol) in anhydrous diethyl ether (20 mL) was added dropwise to a solution of 1-methylethyl cyclopentadienyl anions (15 mmol) in anhydrous diethyl ether at 0 °C. The mixture was stirred overnight at room temperature. The solvent was then reduced to about 10 mL under vacuum. Hexane was added and an orange solid precipitated. The solid was washed with hexane several times and stirred in HCl (5% in water) overnight. The final product was purified by column chromatography on silica gel (CH$_2$Cl$_2$–hexane, 6 : 5) to afford an orange crystalline solid (1.70 g, 65%). IR (KBr pellet) v/cm^{-1}: 3100 (w), 2990 (m), 2930 (w), 2860 (w), 2255 (s), 1615 (s), 1600 (s), 1550 (m), 1510 (s), 1495 (s), 1435 (s), 1415 (s), 1353 (s), 795 (m), 730 (m). ^{1}H NMR (90 MHz, CDCl$_3$, 25 °C, TMS): δ 17.71 (s, 1H, OH), 8.00–7.51 (m, 8H, –C$_6$H$_4$), 7.21 (m, 5H, –C$_6$H$_5$), 6.94 (s, 2H, –C$_5$H$_2$), 2.0 (q, 2H, –CH$_2$), 1.54 (s, 3H, –CH$_3$), 0.8 (t, 3H, –CH$_3$). Elemental analysis. Calc. for C$_{31}$H$_{24}$O$_2$N$_2$: C 82.49, H 5.25, N 6.13. Found: C 81.49, H 5.26, N 6.09%.

Synthesis of 3. AgPF$_6$ (12.8 mg, 0.050 mmol) was added to a solution of **1** (22.8 mg, 0.05 mmol) in 15 mL of benzene. After about 30 min of stirring at room temperature, the mixture was heated under reflux for several minutes. After filtering, the resultant yellow solution was introduced into a 7 mm diameter tube. After standing at room temperature for around one day, orange crystals of **3** were obtained (74%). IR (KBr pellet) v/cm^{-1}: 3500 (br), 3000 (s), 2940 (s), 2860 (w), 2300 (s), 2250 (w), 1610 (s), 1550 (s), 1512 (m), 1432 (m), 1412 (m), 1350 (s), 1172 (m), 1118 (m), 1090 (m), 840 (vs), 800 (w), 726 (w), 698 (m). Elemental analysis. Calc. for C$_{68}$H$_{54}$AgF$_6$N$_4$O$_4$P: C 65.60, H 4.34, N 4.50. Found: C 65.45, H 4.34, N 4.44%.

Synthesis of 4. AgSbF$_6$ (17.2 mg, 0.050 mmol) was added to a solution of **1** (22.2 mg, 0.05 mmol) in 15 mL of benzene. Then xylene (5 mL) and toluene (5 mL) were added. After about 5 min of stirring at room temperature, hexane was added in above mixture until precipitation just occurred. After filtering, and standing at room temperature for around three days, orange crystals of **4** were obtained (64%). IR (KBr pellet) v/cm^{-1}: 3500 (br), 3000 (m), 2850 (m), 2275 (s), 2250 (s), 1620 (s), 1598 (m), 1550 (s), 1490 (m), 1445 (m), 1418 (m), 1370 (s), 1350 (vs), 1200 (s), 1146 (m), 1115 (w), 1092 (m), 728 (s), 654 (s). Elemental analysis. Calc. for C$_{74}$H$_{60}$AgF$_{16}$N$_4$O$_4$Sb: C 55.40, H 3.49, N 2.61. Found: C 55.45, H 3.47, N 2.59%.

Synthesis of 5. A mixture of **1** (45.6 mg, 0.10 mmol) and Co(OAc)$_2$·2H$_2$O (24.9 mg, 0.10 mmol) in anhydrous EtOH (15 mL) was refluxed for 5 min and allowed to cool. The clear red solution was allowed to stand at room temperature for about two days. Deep red crystals of **5** were obtained, washed with hexane and dried in air (78%). IR (KBr pellet) v/cm^{-1}: 3475 (br), 2995 (m), 2255 (s), 1600 (m), 1585 (s), 1560 (vs), 1530 (s), 1494 (s), 1440 (w), 1430 (m), 1415 (s), 1360 (m), 1315 (s), 775 (s). Elemental analysis. Calc. for C$_{66}$H$_{58}$CoN$_4$O$_6$: C 74.57, H 5.46, N 5.27. Found: C 74.50, H 5.49, N 5.14%.

Synthesis of 6. A mixture of **2** (24 mg, 0.054 mmol) and Mn(OAc)$_2$·2H$_2$O (20 mg, 0.027 mmol) in anhydrous EtOH (15 mL) was refluxed for 5 min and allowed to cool. The clear red solution was allowed to stand at room temperature for about three days. Red crystals of **6** were obtained, washed with hexane and dried in air (86%). IR (KBr pellet) v/cm^{-1}: 3500 (br), 2995 (m), 2255 (s), 1600 (m), 1587 (s), 1558 (vs), 1530 (s), 1492 (s), 1451 (w), 1434 (m), 1411 (s), 1343 (m), 1311 (s), 755 (s). Elemental analysis. Calc. for C$_{64}$H$_{54}$N$_4$O$_6$Mn: C 74.56, H 5.24, N 5.44; Found: C 74.50, H 5.26, N 5.34%.

Single-crystal structure determinations

Suitable single crystals of **3–6** were selected and epoxied in inert oil onto thin glass fibers. X-Ray intensity data were measured on a Bruker Smart-1000 CCD and Bruker SMART APEX CCD-based diffractometer system (Mo-Kα radiation, λ = 0.71073 Å). The first 50 frames were recollected at the end of the process to monitor crystal decay; no significant decay was observed in any case. The raw frame data for **3–6** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[32] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[32a] Illustrations were obtained using ORTEP.[32b] All structures were solved by direct methods and refined against F^2 by the full-matrix least squares technique. Hydrogen atoms were calculated and refined as riding atoms; all non-hydrogen atoms were refined with anisotropic displacement parameters. For compound **5**, three components of the molecule were found to be disordered, as follows: (1) Ethyl/methyl group disorder around the chiral carbon C(22), in the refined ratio 0.72(1)/0.28(1); (2) two-fold orientational disorder of the carbon atoms of the coordinated EtOH molecule; (3) a small amount of rotational disorder of the cyanophenyl group {N(1), C(7)–C(13)}. Evidence of the latter disorder arises from the location of the two largest residual electron density peaks (1.28 and 1.18 e Å^{-3}), which correspond to the location of the –CN group after two-fold rotation of the phenyl ring around the C(6)–C(7) bond. However, this disorder was not modeled due to the small percentage of the minor component (<10%). For **6**, one –C$_6$H$_4$CN group of the C$_{30}$H$_{21}$N$_2$O$_2$ ligand was found to be rotationally disordered over two orientations in a 0.671(3)/0.329(3) ratio. Solution and refinement in the space group P1 did not remove the disorder; the space group $P\bar{1}$ was therefore retained. Crystal data, data collection parameters, and refinement statistics for **3–6** are listed in Table 1. Relevant interatomic bond distances and bond angles for **3–6** are given in Tables 2–5.

CCDC reference numbers 210651–210654.

See http://www.rsc.org/suppdata/dt/b3/b310591c/ for crystallographic data in CIF or other electronic format.

Results and discussion

Structural analysis of 1

Ligand **1** was prepared in moderate yield as a deep-yellow crystalline solid by the reaction of 3-cyanobenzoyl chloride with corresponding alkyl-substituted cyclopentadienyl anions, which derived from 6-methyl-6′-ethylenefulvene and phenyllithium in diethyl ether at 0 °C (Scheme 1). Ligands **1** is very soluble in common organic solvents, such as CH$_2$Cl$_2$, CHCl$_3$, THF and C$_6$H$_6$. The structure of **1** was determined by ^{1}H NMR, IR and elemental analysis. The IR spectrum of **1** showed a –CN absorption band at 2255 cm^{-1}. In the ^{1}H NMR spectrum of **1**, the proton resonance were observed at 17.71 ppm as a singlet. It is attributed to the chelated proton, which is hydrogen bonded to the neighbor carbonyl on the 1-benzoyl group.[26,33] The IR spectrum of **1** does not show absorption above 1630 cm^{-1} in the region normally assigned to organic carbonyl groups. However, the strong absorption band at 1615 cm^{-1} is consistent with the hydrogen-bonded enol structure, since it has been shown that conjugation and chelation lead to a large shift of the carbonyl infrared band. Thus compound **1** exists in the form of fulvene,[26,33] which is one of the most important moieties in organometallic chemistry.[34] In addition to the two –CN groups, the carbonyl and enol groups in **1** could act as potential chelating coordinating sites to bind transition metal

Table 1 Crystallographic data for **3–6**

Empirical formula	$C_{37}H_{30}Ag_{0.5}F_6N_2O_2P$, **3**	$C_{44}H_{38}Ag_{0.5}F_6N_4O_4Sb$, **4**	$C_{66}H_{58}CoN_4O_6$, **5**	$C_{32}H_{27}Mn_{0.5}N_4O_6$, **6**
M_r	1243.99	1412.89	1062.09	1030.05
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.209(3)	8.148(3)	9.0135(6)	8.6786(4)
b/Å	11.951(4)	13.607(4)	10.8860(7)	10.8010(5)
c/Å	15.384(5)	15.390(5)	14.6113(10)	14.5929(7)
α/°	103.007(6)	108.439(5)	100.3850(10)	93.6690(10)
β/°	94.673(6)	94.268(6)	101.2500(10)	99.7260(10)
γ/°	94.643(6)	94.948(6)	91.2150(10)	94.2720(10)
V/Å³	1458.0(8)	1603.3(9)	1380.73(16)	1340.41(11)
Z	1	1	1	1
D_c/g cm^{-3}	1.417	1.463	1.277	1.276
μ(Mo-Kα)/mm^{-1}	0.250	0.620	0.368	0.152
T/K	293	293	150	150
Data/restraints/param.	5773/0/382	5603/14/409	3959/4/370	5475/3/366
$R1$; $wR2$ indices ^{a} (all data)	0.1804; 0.1211	0.1958; 0.2012	0.0830; 0.1864	0.0504; 0.1067

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **3**

Ag(1)–N(1)	2.193(4)	Ag(1)–N(2)#2	2.622(4)
N(1)–Ag(1)–N(1)#1	180	N(1)–Ag(1)–N(2)#2	86.79(14)
N(2)#2-Ag(1)–N(2)#3	180	C(14)–N(1)–Ag(1)	159.0(4)
C(21)–N(2)–Ag(1)#4	127.1(4)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y, -z + 2$. #2 $-x + 1, -y, -z + 1$. #3 $x + 1, y, z + 1$. #4 $x - 1, y, z - 1$. #5 $-x, -y + 1, -z$. #6 $-x + 1, -y + 1, -z + 1$.

Table 3 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **4**

Ag(1)–N(2)#2	2.192(7)	Ag(1)–N(1)	2.597(8)
N(2)#2–Ag(1)–N(2)#3	180	N(2)#2–Ag(1)–N(1)	92.5(3)
N(1)–Ag(1)–N(1)#4	180	C(14)–N(1)–Ag(1)	124.6(7)
C(21)–N(2)–Ag(1)#5	160.8(8)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$. #2 $x + 1, y, z + 1$. #3 $-x + 2, -y + 2, -z$. #4 $-x + 3, -y + 2, -z + 1$. #5 $x - 1, y, z - 1$.

Table 4 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **5**

Co–O(2)#1	2.005(3)	Co–O(1)	2.019(3)
Co–O(3)#1	2.137(3)		
O(2)#1–Co–O(2)	180	O(2)#1–Co–O(1)	89.23(11)
O(1)–Co–O(1)#1	180	O(2)#1–Co–O(3)#1	88.36(12)
O(2)–Co–O(3)#1	91.64(12)	O(1)#1–Co–O(3)#1	94.48(12)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$.

Table 5 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **6**.

Mn–O(1)	2.0856(11)	Mn–O(2)	2.1035(12)
Mn–O(3)	2.2187(13)		
O(1)–Mn–O(1)#1	180	O(1)–Mn–O(2)#1	92.25(5)
O(2)#1–Mn–O(2)	180	O(1)–Mn–O(3)	88.73(5)
O(2)#1–Mn–O(3)	86.38(5)	O(1)#1–Mn–O(3)#1	88.73(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$. #2 $-x, -y + 2, -z + 1$.

ions into seven-membered metallo-ring containing complexes; they could also be potentially transferred to other types of organic functional groups, such as heterocyclic rings, by reaction with hydroxylamine, hydrazine or the like. Compound **1** can be classified as a new type of ligand that can be used for the construction of polymeric compounds containing both inorganic and organometallic moieties. The synthesis of **2** and its X-ray single crystal molecular structure will be published elsewhere.

Structural analysis of 3

Silver-containing polymeric compound **3**, namely [Ag(**1**)$_2$-(PF$_6$)]·C$_6$H$_6$ was synthesized by combination of **1** and AgPF$_6$ in benzene at ambient temperature in 74% yield. Crystals of **3** lose solvent molecules and turn opaque within several minutes under ambient atmosphere. Due to its instability, the host–guest chemistry of **3** could not be investigated. Compound **3** crystallizes in the triclinic space group $P\bar{1}$. Single crystal analysis revealed, as shown in Fig. 1, each Ag(I) center in **3** is located on an inversion center and is four-coordinate, showing a rhombic planar geometry (Ag(1)–N(1) 2.193(4), Ag–N(2) 2.622(4) Å; N(1)–Ag–N(2) 180 and N(1)–Ag(1)–N(2)#2 86.79(14)°). Two uncoordinated crystallographically equivalent PF$_6^-$ counter ions lie on an inversion center and are located above and below the {AgN$_4$} plane. The shortest Ag $\cdots$ F contact is 4.499(4) Å. In addition, there is one solvent benzene

molecule per formula in **3**, which is located on another inversion center.

In the solid state, Ag(I) centers are connected to each other by four ligands **1** into novel one-dimensional undulating chains extending along the crystallographic c axis (Fig. 2). The individual "links" in the chains consist of Ag$_2$(**1**)$_2$ units, which can be viewed as 32-membered rings enclosed by two Ag(I) atoms and two ligands of **1**. The approximate (crystallographic) dimensions of the rings are 17 × 6 Å. The benzene molecules are located between these cage rings (Fig. 2). The intrachain and interchain Ag $\cdots$ Ag separation is 16.837(5) and 11.951(3) Å (b-cell dimension), respectively. It is noteworthy that ligand **1** is a chiral molecule, though the coordination polymers crystallized in a centrosymmetric space group $P\bar{1}$, due to the 1 : 1 arrangement of R- and S-configurations in **3**.

Structural analysis of 4

Silver-containing polymeric compound **4**, namely [Ag(**2**)$_2$-(SbF$_6$)]·2C$_7$H$_8$ was synthesized by combination of **1** and AgPF$_6$ in xylene–toluene at ambient temperature in 64% yield. Crystals of **4** lose solvent molecules and turn opaque within several minutes under ambient atmosphere. Due to its instability, the host–guest chemistry of **3** could not be investigated. Single crystal analysis revealed, as shown in Fig. 3, that **4** is isostructural with **3** except that the ligand **1** is replaced by **2**. Each Ag(I) center in **4** also lies on an inversion center and adopts a {AgN$_4$} rhombic planar coordination sphere (Ag(1)–N(1) 2.597(8) and
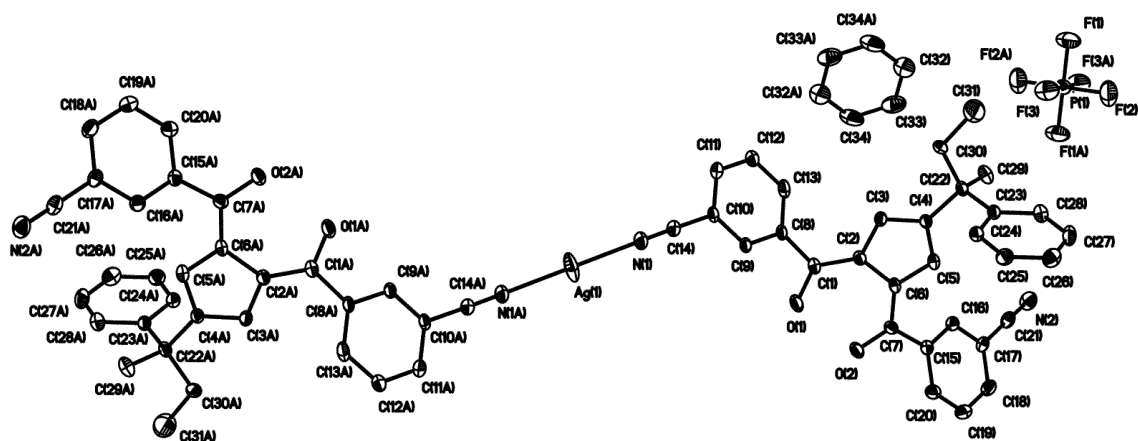
Fig. 1 ORTEP illustration of compound **3** (asymmetric unit) with 30% probability ellipsoids.
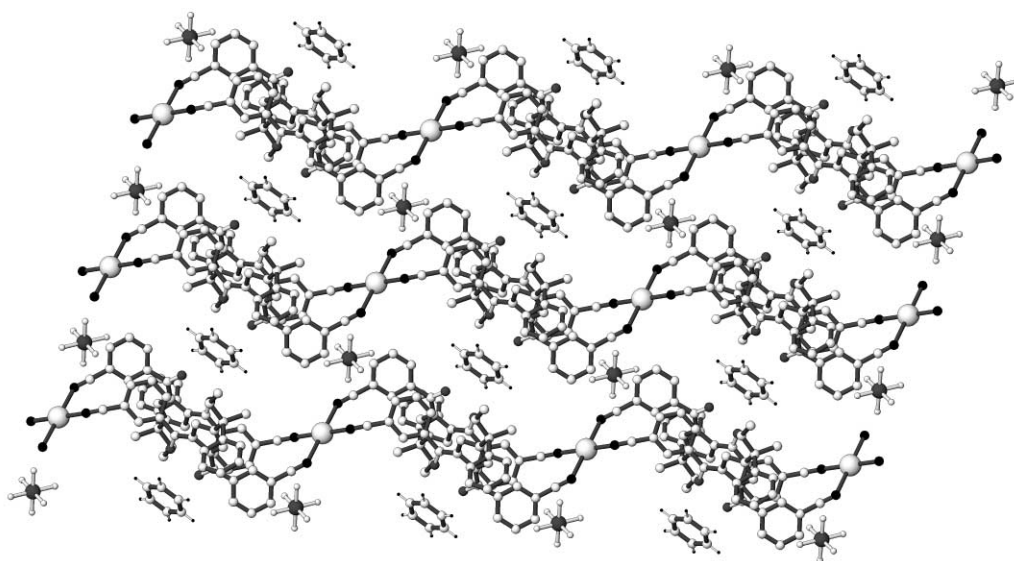

Fig. 2 Crystal packing of **3** (three one-dimensional chains consisting of Ag$_2$(**1**)$_2$ units).
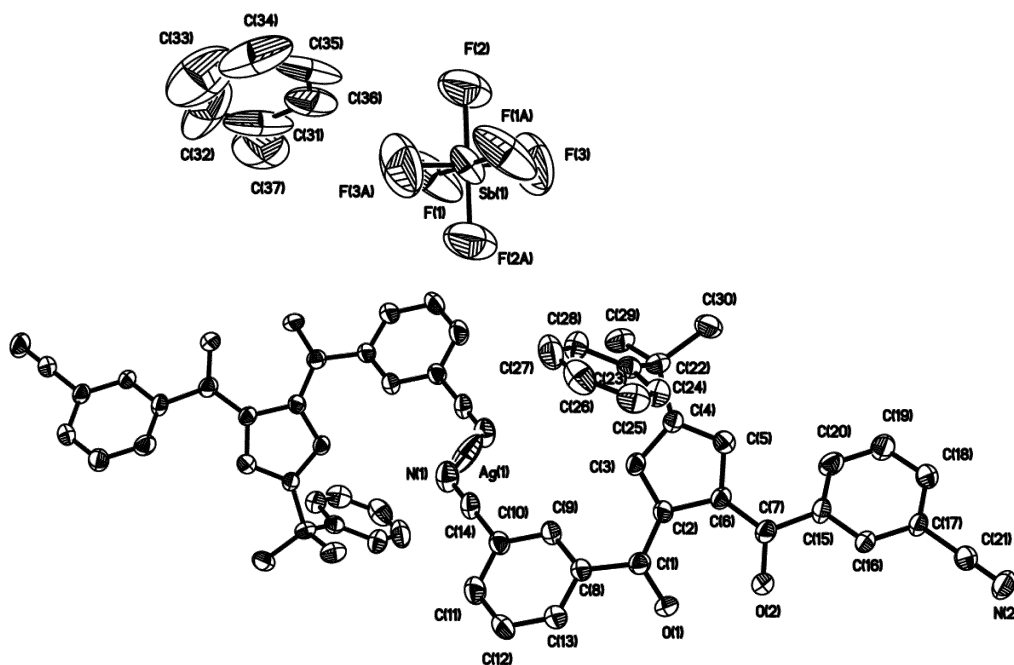

Fig. 3 ORTEP illustration of compound **4** (asymmetric unit) with 30% probability ellipsoids.

Ag(1)–N(2) 2.192(7) Å; N(2)#2–Ag(1)–N(2)#3 180 and N(2)#2–Ag(1)–N(1) 92.5(3)°). Two uncoordinated crystallographically equivalent SbF$_6^-$ counter ions lie on an inversion center and are located above and below the {AgN$_4$} plane. The shortest Ag $\cdots$ F contact is 4.965(4) Å, which is slightly longer than that of in **1**.
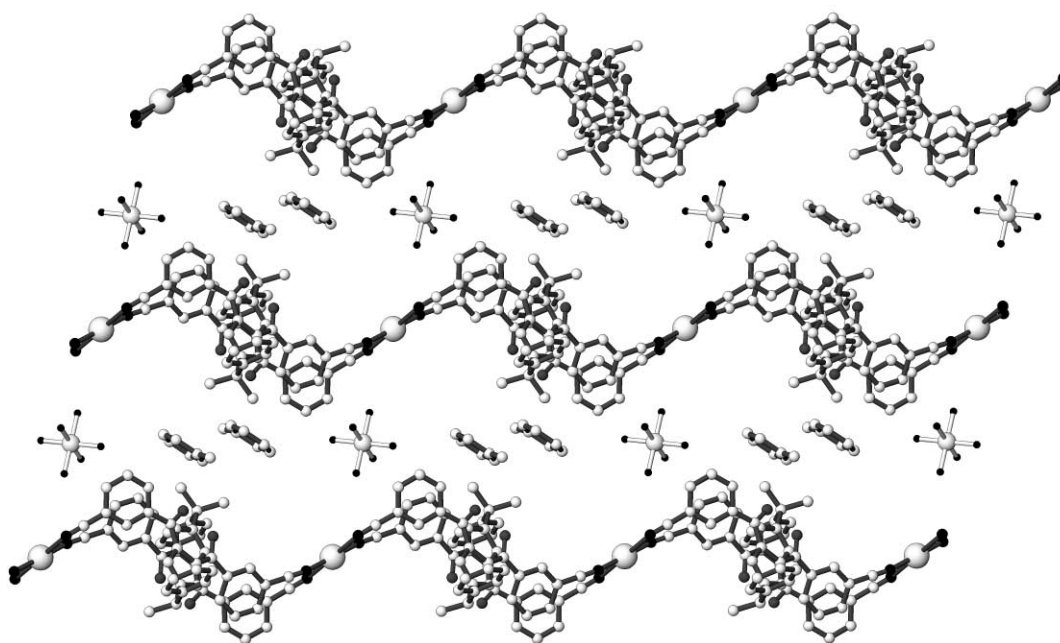
Fig. 4 A side-on view of the one-dimensional chains in **4**; SbF_6^- and toluene molecules are located between the chains.

Compared to **1**, a similar one-dimensional undulating chain was found in **2** which consists of $Ag_2(2)_2$ units (crystallographic dimensions, *ca.* 17 × 4 Å). The uncoordinated SbF_6^- counter ions and guest toluene molecules are located between the chains (Fig. 4). No interchain hydrogen binding interactions were found. The intra- and interchain Ag · · · Ag distances are 16.869(4) and 13.607(4) Å, respectively.

As noted above, ligands **1** and **2** adopt transoid conformations to coordinate Ag(I) centers in **3** and **4**. The *trans*-conformation orients the two –CN groups in two different directions, and does not allow them to converge at the neighboring metal center in the linear chain. Of course, it is still not clear why the ligands do not simply adopt another structure, such as a higher dimensional framework motif, though the steric influence of the large substituted groups on the Cp-rings during the self-assembly process probably plays a role. It is worthwhile to point out that, in these specific reactions, the products do not depend on of the ligand-to-metal ratio. However, increasing the ligand-to-metal ratio resulted in somewhat higher yield and higher crystal quality.

Structural analysis of 5 and 6

The complexes **5** and **6** were synthesized by solution reactions between the new ligands **1** and **2** and $Co(OAc)_2 \cdot 2H_2O$ and $Mn(OAc)_2 \cdot 2H_2O$ in ethanol, respectively. When a solution of ligands **1** and **2** in ethanol were treated with $M(OAc)_2 \cdot 2H_2O$ (M = Co(II) and Mn(II)), respectively, in a metal-to-ligand molar ratio of 1 : 2, compounds **5** and **6** were obtained as the neutral molecular compounds with seven-membered metallo-rings. It is worth pointing out that the coordination chemistry of **1** and **2** with transition metal templates Cu(II) and Co(II) are independent of the metal-to-ligand mole ratio. For example, when the metal-to-ligand ratio was changed from 1 : 1 to 2 : 1, and even 3 : 1, the compounds **5** and **6** are always isolated as the only products.

Compounds **5** and **6** are isostructural and crystallize in the triclinic system. Both Co(II) and Mn(II) centers are on the inversion centers. As shown in Fig. 5, for example, the Co(II) center lies in a octahedral coordination environment defined by four O-donors from two bidentate ligand **1** and two O-donors from two coordinated ethanol solvent molecules. The octahedral coordination polyhedron is slightly distorted, where all angles around the copper center deviate significantly from 90° (O(2)–Co–O(1) 89.23(11), O(2)#1–Co–O(3)#1 88.36(12),
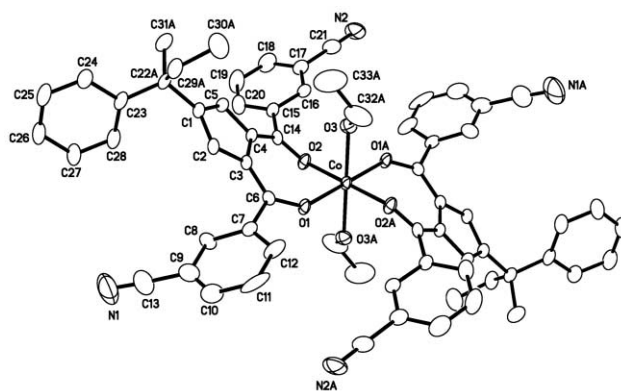
Fig. 5 ORTEP illustration of compound **5** with 30% probability ellipsoids.

O(1)–Co–O(3)#1 85.52(12)°). The Co–O bond distances on the basal plane are 2.005(3) and 2.019(3) Å, respectively, which compare well with the Co–O distance found in cobalt–oxygen complexes.[35] The distances between the cobalt center atom and the two axial O-donor atoms are the same (d_{Co-O} = 2.137(3) Å), again consistent with corresponding bond lengths in complexes with similar coordination environments.[35] It is well known that neutral or deprotonated 1,2-diketone or 1,3-diketone compounds can act as chelating ligands to bind transition metal ions into five- or six-membered metallo-ring systems which engender less strain (Scheme 2),[36] because the atoms on the rings are allowed to adopt more closely their natural bond angles. Seven-membered metallo-ring complexes generated from neutral or deprotoned 1,4-diketone-containing ligands and transition metal ions are much less known probably due to the conformational strain effect.[36] However, there are still some
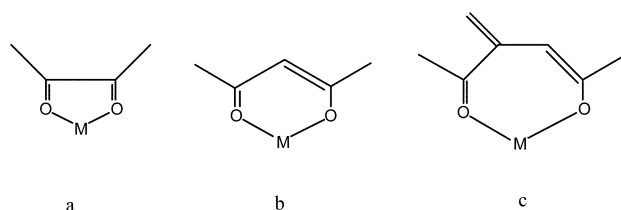
Scheme 2 (a) Five-, (b) six-, and (c) seven-membered metallo-rings adopted by diketone ligands.

interesting seven-membered metallacycle complexes reported recently, such as metal complexes generated from TADDOL,[36b] diazoacetate,[36c] bis(phosphane) ligands,[36d] and related bidentate chelating ligands.[36e] Some of these are demonstrated to be very useful catalysts in metal-catalyzed stereoselective syntheses. Ligand **1** reported herein presents an additional perfect example for the synthesis of seven-membered metallo-ring transition metal complexes because of its specific molecular geometry. In **5**, the carbon–carbon bond distances on the substituted Cp-ring and also its exocyclic carbon–carbon double bonds are almost the same as their corresponding bond lengths in the free ligand **1** (ranging from 1.393(2) to 1.457(2) Å). The four –CN groups in **5** are uncoordinated and every two of them is oriented in the same direction, but in the reserve directions to each other. The IR spectrum of **4** shows that the –C≡N stretch (2255 cm^{-1}) in **5** was essentially unchanged from free ligand **1**, which can be taken as evidence for the nitrile nitrogen not entering the coordination sphere of the Co(II) center. A similar phenomenon occurs in the reaction of $Ru_2(O_2C(CH_2)_6CH_3)_4$ in toluene and $Cu(hfacac)_2 \cdot H_2O$ (hfacac = hexafluoroacetylacetonate) in methylene chloride with 4-cyanopyridine and 3-cyanopyridine, respectively.[37] The discrete molecular 1 : 2 adduct $Ru_2(O_2C(CH_2)_6CH_3)_4$(4-cyano-pyridine)$_2$ and $Cu(hfacac)_2$(3-cyanopyridine)$_2$ are obtained instead of the expected 4-cyanopyridine and 3-cyanopyridine bridged transition metal complexes. It is known that 4-cyano-pyridine, and 3-cyanopyridine spacers have been used as bridging ligands to link transition metal species into dimers and polymers.[38,39] It appears that the nitrile N-donor atom has a poor coordinating ability to effectively link 3d metal ions. For example, in $[(Cu(4\text{-cyanopyridine})_4(H_2O)(ClO_4)_2)]_n$, the nitrile nitrogen only weakly coordinates with copper centers through a "semi-coordinated" bond (Cu–N≡C 2.649(4) Å), which is much longer than a normal Cu–N coordinative bond.[40] It is worth noting that **5** contains uncoordinated N-donors, and could be used as a potential new metal-containing building block, as suggested recently.[41] These building blocks could be connected by other suitable metal ions (Ag^+ or Cd^{2+}, for example) or unsaturated metal complexes *via* bonding inter-actions with the free nitrile nitrogen atoms in **5**, a direction we are pursuing. The shortest Co · · · Co distance is 10.89(3) Å.

In **6**, the Mn(II) center also adopts a distorted octahedral {MnO_6} coordination sphere, which is similar to that of in **5**. The Mn-O bond distances lie in the range of 2.08–2.22 Å, which is comparable to corresponding bond lengths found in known Mn(II)-complexes.[35]

In the solid state, the same H-bonded one-dimensional chain motif is found in both **5** and **6**. For example, for compound **5**, as shown in Fig. 6, the neutral building blocks **5** arrange parallel to the crystallographic *b* axis, and moreover are bound together by strong intermolecular N · · · O–H hydrogen bonds to create a one-dimensional chain motif along the crystallographic *b* axis.[42–44] The hydrogen-bonding systems in **5** and **6** consist of one uncoordinated nitrogen atom on –CN group with the hydrogen atom on the coordinated ethanol molecule oxygen atom of a neighboring M(II) (M = Co for **5** and Mn for **6**) complexes. The N · · · H distances are 2.097(8)
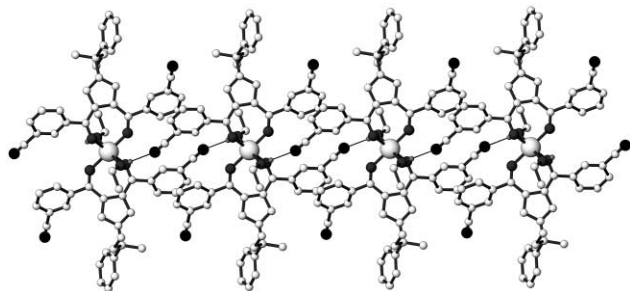
and 1.935(8) Å, respectively. The corresponding O · · · N distances are 2.891(2) and 2.839(2) Å, respectively, and the corresponding O–H · · · N angles are 173(4) and 171(3)°, respectively. The existence and structural importance of strong hydrogen-bonding interactions generated from –CN (as the hydrogen-bond acceptor) are now well established and observed in many compounds.[45] There is no doubt that these strong hydrogen-bonding interactions contribute significantly to the alignment of the molecules of **5** and **6** in the crystalline state. The intrachain Co · · · Co and Mn · · · Mn distances are 10.89(3) and 10.80(3) Å, respectively.

Conclusions

One new fulvene-type ligand **1** was synthesized successfully by aroylation reaction of substituted cyclopentadienyl anions. The coordination chemistry of **1** and **2** have been investigated. The study demonstrated that these new fulvene-type ligands could be used as bidentate or chelating ligands to coordinate transition metal ions into coordination polymers or supra-molecular complexes. Two novel one-dimensional Ag(I)–fulvene coordination polymers containing the Ag$_2$(ligand)$_2$ unit, and two M(II) (M = Co(II) and Mn(II)) complexes with unusual seven-membered metallo-ring units, were synthesized successfully based on them. In the solid state, complexes **5** and **6** adopt a novel hydrogen-bonded one-dimensional chain motif. We are currently extending this result by preparing new fulvene ligands of this type with different substituted organic func-tional groups. We anticipate this approach to be useful for the construction of a variety of new transition-metal complexes and coordination polymers (including bimetallic polymeric compounds) with novel structures.

Acknowledgements

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Fig. 6 Hydrogen-bonded one-dimensional chain in **5** and **6**.

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