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Metal-Dependent Formation of Mononuclear Complexes and M_2L_2 Mesocates with Schiff-Base Ligands

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The coordination chemistry of the tetradentate pyridyl N-donor ligands *r*-1-hydroxy-*t*-3,*t*-5-bis{[(2-pyridinyl)methylene]amino}cyclohexane (DDOP) and *r*-1-hydroxy-*t*-3,*t*-5-bis{[(*E*)-(6-methyl-2-pyridinyl)methylene]amino}cyclohexane (DDMOP) has been investigated with the d^{10} metal centres silver(I) and cadmium(II). These conformationally flexible ligands offer two coordination modes; either a mononucleating tetradentate coordination pocket or a bridging bis(bidentate) chelate. Hence, reaction with Cd^{II} produced six-coordinate mononuclear complexes whose compositions were determined by X-ray crystallography as $[Cd(DDOP)(NO_3)_2]$ (**1**) and $[Cd(DDMOP)(Cl)_2]$·MeOH (**2**), while Ag^I led to the four-coordinate dinuclear mesocate structures $[\{Ag(DDOP)\}_2](CF_3SO_3)_2$ (**3**) and $[\{Ag(DDMOP)\}_2](CF_3SO_3)_2$·0.5MeOH (**4**). It is thought that the mononuclear, octahedral complexes in the case of zinc(II) and cadmium(II) result from the energetic stabilisation gained through two extra coordinate bonds, while in the case of silver(I) the lower propensity of the metal centre for six-coordination causes the ligand to retain its energetically preferred dinucleating conformation and to form the mesocates.

Introduction

Control over the nuclearity and shape of coordination complexes has been a vital topic in inorganic chemistry for decades, most particularly since the emergence of supramolecular chemistry in the late 1970s, and provides the key to future development of designed functional materials.[1–3] Through careful choice of ligand topology, numerous research groups have been able to control formation of oligomeric and polymeric structures; for example the formation of double- and triple-stranded helicates/mesocates,[4–6] molecular squares and boxes,[7,8] and infinite inorganic grids.[9,10] Such chemistry often relies on the use of large, rigid aromatic N-donor sets, for example the various bi- and terpyridines, linked by spacers whose shape and rigidity (or relative flexibility) determines the type of complex. Schiff-base derivatisation of aliphatic amines or anilines with pyridinecarbaldehydes provides an attractive route to aromatic N-donor ligands, due to the relative synthetic ease of this transformation and the availability of many different parent amines.[11]

Recent work in our laboratory has focused on the synthesis and coordination behaviour of the small, cyclohexane-based aliphatic amino ligands *r*-1,*t*-3,*t*-5-triaminocyclohexane (TACH)[12–14] and *t*-3,*t*-5-diamino-*r*-1-hydroxycyclohexane (DAHC).[15–17] While becoming rigid upon coordination due to conformational locking of the cyclohexane backbone, these ligands offer two coordination modes; either bridging with the *cis*-diamino donor set in the equatorial plane, or bidentate chelating upon "ring-flip" to the bis(axial) conformation. Derivatisation of the amine groups of these ligands with Schiff bases allows the synthesis of pyridyl N-donor ligands which, like their parent amines, possess two distinct coordination modes. Such ligands may form complexes with different nuclearity according to the coordination preferences of the metal centre.[18,19] Herein, we describe mono- and dinuclear coordination complexes of the DAHC Schiff-base derivatives *r*-1-hydroxy-*t*-3,*t*-5-bis{[(2-pyridinyl)methylene]amino}cyclohexane (DDOP) and *r*-1-hydroxy-*t*-3,*t*-5-bis{[(*E*)-(6-methyl-2-pyridinyl)methylene]amino}cyclohexane (DDMOP) with the d^{10} transition-metal ions Cd^{II} and Ag^I.

Results and Discussion

Overview

DDOP and DDMOP were synthesised from DAHC by a simple Schiff-base derivatisation using the appropriate pyridinecarbaldeyhyde, yielding a more highly pre-organised ligand with a tetradentate [or bis(bidentate)] donor set. The aromatic rings increase the system's rigidity, strengthening the hand of the ligand and reducing the influence of anions, solvent and metal centres on the outcome of the complexation. Furthermore, they provide a hydrophobic surface capable of participating in π-stacking or other van der Waals interactions.

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Despite the rigidity of the donor set, the conformational flexibility of the cyclohexane backbone gives these ligands two possible coordination modes (Scheme 1); either as a dinucleating, bis(bidentate) chelator, or a bis(axial) tetradentate mononucleating conformation. Both coordination modes are observed in this study, the dinuclear compounds being formed with silver(I) and mononuclear, ring-flipped compounds occurring with cadmium(II). The ligands direct the formation of M_2L_2 mesocate structures when in their bis(equatorial) conformation, since the two N_2 donor sets are suitably oriented to bind to one side of the metal–metal axis, and the angle of approximately 105° between the planes of the aromatic rings provides an effective corner piece. Consequently, formation of dinuclear complexes is favoured by four-coordinate, tetrahedral metal centres whose ca. 90° twist angle provides a good geometric match for the bis(equatorial) ligand. Mononuclear species are favoured by coordination to octahedral metal centres, whose equatorial sites can accept the planar N_4 donor set of the bis(axial) ligand, with their axial sites being occupied by solvent molecules or counterions. Formation of the two types of complexes is described by the balanced equations below, which summarise the reaction of two metal centres with two ligands:

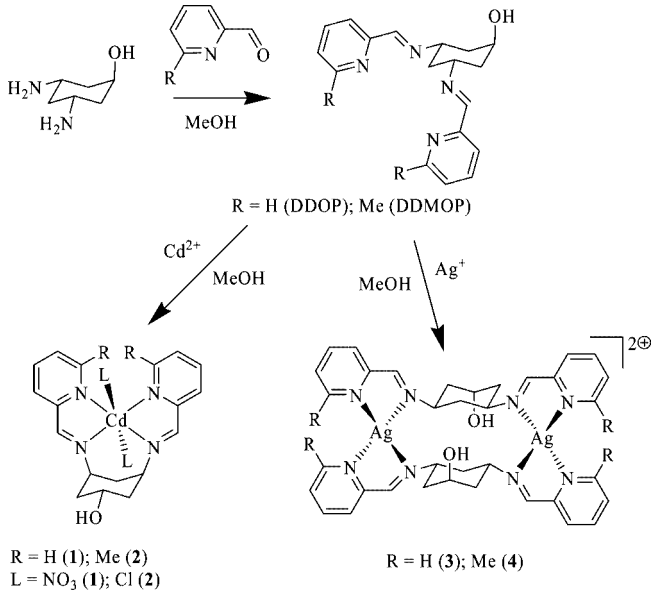
Dinuclear complex:

$2\ MX_2{\cdot}nH_2O + 2\ L \rightarrow M_2L_2^{4+} + 4\ X^- + 2n\ H_2O$; $(2n + 5)$ species, 8 coordinate bonds.

Mononuclear complex:

$2\ MX_2{\cdot}nH_2O + 2\ L \rightarrow 2\ MLX_2 + 2n\ H_2O$; $(2n + 2)$ species, 12 coordinate bonds.

For silver(I) and cadmium(II), which can access both tetrahedral and octahedral coordination geometries, the two reactions are in competition with each other. It can be seen from the larger number of species formed that four-coordinate M_2L_2 structures are favoured due to entropic factors; furthermore, the bis(equatorial) ligand conformation observed in such complexes is more energetically favourable due to reduced steric clash between the imine arms and the cyclohexane ring. However, the extra coordination bonds formed in the mononuclear case means that these complexes are favoured by enthalpy.



Scheme 1. Parent amine DAHC, and mono- and dinuclear species formed by complexation of its Schiff-base derivatives DDOP and DDMOP.

Cadmium(II) Complexes

Cadmium(II) complexes of DDOP and DDMOP were prepared in moderately low yields by reaction with cadmium(II) salts (nitrate or chloride) in methanol, followed by crystallisation by diffusion of diethyl ether. This yielded the (DDOP)bis(nitrato)cadmium complex [Cd(DDOP)-$(NO_3)_2$] (**1**), and the (DDMOP)bis(chlorido)cadmium complex [Cd(DDMOP)Cl_2]·MeOH (**2**) (the DDMOP complex would not crystallise with the nitrato ligand). In both, the N_4 ligand acts as a tetradentate chelator in the equatorial plane, while the chlorido or nitrato ligands occupy the axial coordination sites (Figure 1). However, interestingly, the asymmetric unit of **1** contains two crystallographically independent complexes, which appear to be associated with each other through a slipped π-stacking interaction with a centroid-to-centroid distance of around 3.80 Å.

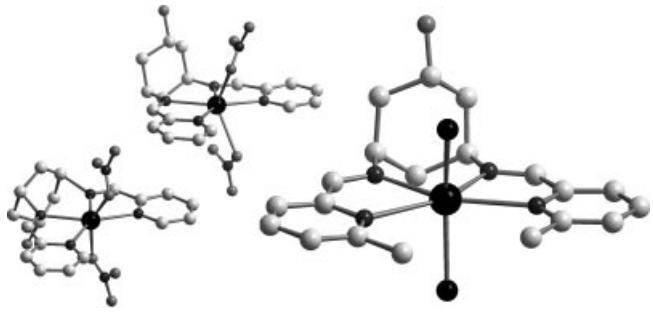


Figure 1. The two [Cd(DDOP)$(NO_3)_2$] complexes in the asymmetric unit of **1** (left) and the complex in [Cd(DDMOP)$(Cl)_2$]·MeOH (**2**). C: light grey; N: dark grey; O: medium grey; Cl: small black spheres; Cd: large black spheres; H: omitted.

Curiously, the pair of complexes in **1** differs quite noticeably in its Cd–O bond lengths; Cd2 has longer bonds to the oxygen atoms, and shorter bonds to the equatorial nitrogen atoms (Table 1). The size of the cadmium cation causes the pyridyl arms of the ligand to open from their idealised parallel alignment, as indicated by longer coordination bonds to the pyridyl nitrogen atoms, and also by an N–Cd–N angle that is much larger between the pyridyl nitrogen atoms than the imino nitrogen atoms. This effect is more dramatic in **2**, where replacement of hydrogen with a methyl group at the 6-position of the pyridyl ring forces the imine arms to open wider to accommodate the increased steric demand (Figure 1). Bond lengths to the axial chlorido ligands are comparable to the axial Cd2–O bond lengths in compound **1**. In solution, ^{1}H NMR spectroscopy (CD_3OD) reveals the ring-flipped structure of these complexes, as shown by the

Table 1. Selected bond lengths [Å] and angles [°] in [Cd(DDMOP)$(NO_3)_2$] (**1**) and [Cd(DDMOP)Cl_2]·MeOH (**2**). L_{eq} = NO_3 or Cl.

	Compound **1**, Cd1	Compound **1**, Cd2	Compound **2**
$Cd–N_{im}$	2.316(13), 2.327(13)	2.316(13), 2.321(13)	2.376(2), 2.415(2)
$Cd–N_{py}$	2.349(11), 2.372(12)	2.332(11), 2.354(14)	2.499(2), 2.600(2)
$N_{py}–Cd–N_{py}$	132.4(4)	132.9(4)	139.97(8)
$N_{im}–Cd–N_{im}$	82.9(4)	83.8(5)	82.97(8)
$Cd–L_{eq}$	2.381(13), 2.475(17)	2.50(3), 2.506(14)	2.500(1), 2.530(1)
$L_{eq}–Cd–L_{eq}$	164.3(6)	153.4(5)	139.97(8)

multiplicities of the cyclohexane protons which provide an excellent conformational probe. Identical NMR spectra were obtained by directly dissolving the ligand and a small excess of the cadmium salt in CD_3OD, indicating that the low yields are due to inefficient crystallisation, rather than formation of other architectures. Furthermore, coordination to Cd is indicated by satellites resulting from coupling of the imine protons to the I = 1/2 isotopes ^{111}Cd and ^{113}Cd (combined abundance = 25%).

The differing shapes and hydrogen-bonding properties of the chlorido and nitrato ligands result in contrasting extended structures for the two compounds. In **1** there are alternating layers of the two crystallographically independent complexes (Figure 2), in which they associate in chains parallel to the crystallographic *c*-axis through hydrogen-bonding interactions between the nitrato ligands and the DDOP alcohol groups (2.976 Å in the Cd1 layer). However, in the Cd2 layers the nitrato–hydroxy distance (3.126 Å) is longer than the sum of the van der Waals radii. Association of the layers appears to occur by the π-stacking interactions observed in the asymmetric unit. In **2**, the [Cd(DDMOP)-Cl_2] units are arranged in hydrogen-bonded chains parallel to the crystallographic *b*-axis (Figure 2). To generate the chains, one chlorido ligand accepts a hydrogen bond from the DDMOP alcohol group (3.195 Å) of the next complex, and the other chlorido ligand accepts a hydrogen bond from an included methanol molecule (3.140 Å). The pyridyl–pyridyl separations observed are too large to suggest any significant contributions from π-stacking.

To investigate the influence of temperature on these complexations, reactions were also performed at –94 °C, –78 °C, and in refluxing *n*-propanol (97 °C). It was anticipated that low temperatures might reduce the conformational flexibility of the ligand, encouraging formation of dinuclear aggregates on kinetic grounds, while higher temperatures would increase the influence of entropy, again favouring dinuclear species. However, ^1H NMR revealed that mononuclear species still result under these conditions.

Silver(I) Complexes

In contrast to cadmium(II), complexation of DDOP and DDMOP with silver(I) results in the formation of M_2L_2 mesocates, synthesised in analogous fashion to the cadmium complexes by reaction with silver(I) triflate. The $M_2L_2^{2+}$ complex cations are formed by two ligands in the bis(equatorial) conformation, linked by two Ag(1) centres with distorted pseudo-tetrahedral geometries (Figure 3). These dinuclear structures occur because the octahedral coordination mode is less accessible for silver(I) than cadmium(II), and because nonplanar geometries are favoured by four-coordinate silver atoms.[18] Furthermore, the bis-(equatorial) coordination mode is more favourable for the ligand as it minimises steric clashes between the pyridyl and cyclohexane rings. ^1H NMR (CD_3OD) reveals the M_2L_2 form of the complexes upon dissolution, and while coupling of the imine protons to the silver ion (I = 1/2) is only observed in **4**, the change in chemical shift relative to uncomplexed ligand suggests that **3** does not dissociate. Identical spectra obtained simply by mixing the silver salt and ligand in CD_3OD suggest that the low yield obtained for **3** is due

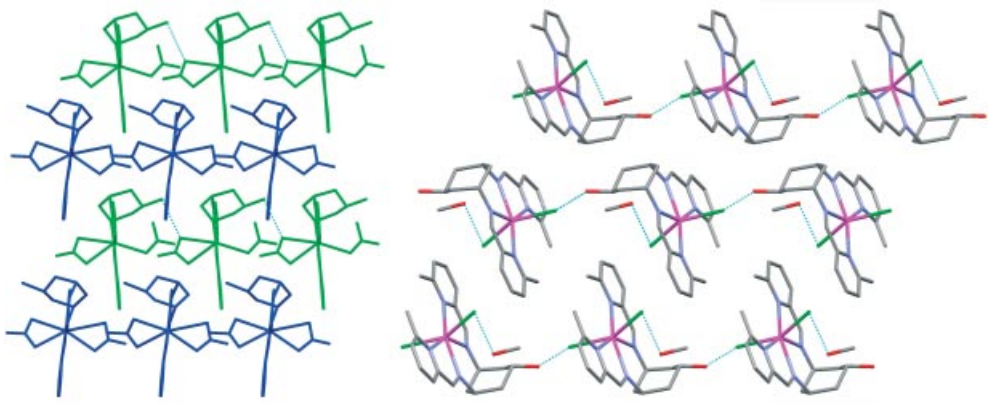


Figure 2. Crystal packing and hydrogen bonding in [Cd(DDOP)$(NO_3)_2$] (**1**, left) and [Cd(DDMOP)Cl_2]·MeOH (**2**, right). In **1**, Cd1 complexes are green and Cd2 blue; colour scheme in **2**: C grey; N blue; O red; Cl green; Cd purple; H omitted. Hydrogen bonds are shown as bright blue dotted lines.

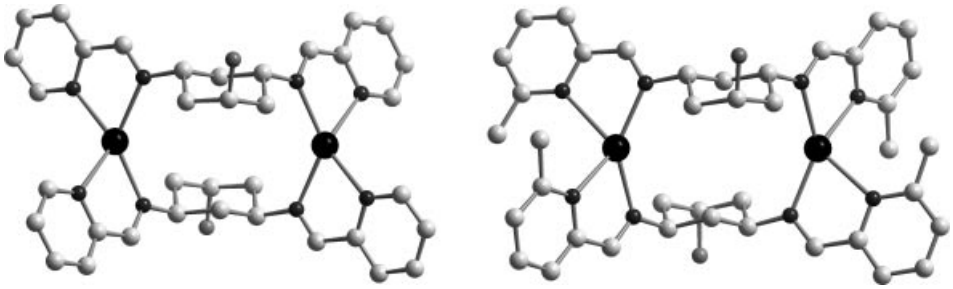


Figure 3. Complex cations in $[\{Ag(DDOP)\}_2](CF_3SO_3)_2$ (**3**) and $[\{Ag(DDMOP)\}_2](CF_3SO_3)_2 \cdot 0.5MeOH$ (**4**). Ag black, C light grey; N dark grey; O medium grey; H omitted.

Table 2. Bond lengths [Å] and angles [°] in $[\{Ag(DDOP)\}_2](CF_3SO_3)_2$ (**3**) and $[\{Ag(DDMOP)\}_2](CF_3SO_3)_2 \cdot 0.5MeOH$ (**4**).

	Compound **3**	Compound **4**
Ag(1)–N	2.236(4), 2.290(4), 2.342(5), 2.438(5)	2.241(5), 2.250(4), 2.410(5), 2.427(5)
Ag(2)–N	N/A	2.209(4), 2.287(4), 2.357(5), 2.549(5)
N–Ag(1)–N	133.18(15), 141.50(19), 73.05(17), 72.40(16), 127.99(16), 117.00(17)	141.72(17), 139.35(16), 72.17(16), 73.02(17), 129.48(16), 103.35(17)
N–Ag(2)–N	N/A	140.93(17), 138.44(16), 72.31(17), 71.42(16), 134.37(15), 103.34(16)

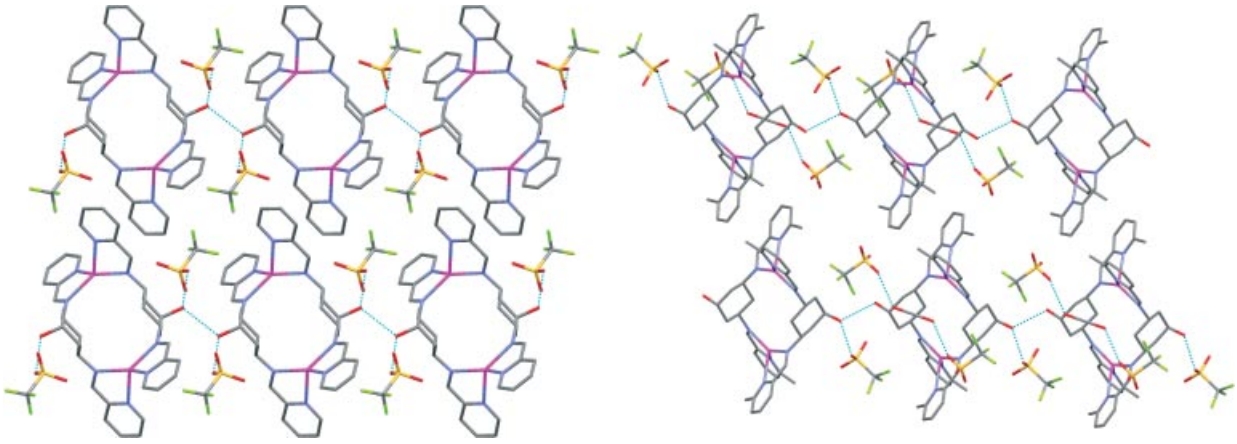


Figure 4. Crystal packing in $[\{Ag(DDOP)\}_2](CF_3SO_3)_2$ (**3**, left) and $[\{Ag(DDMOP)\}_2](CF_3SO_3)_2$ (**4**, right). S yellow; F light yellow; Ag purple; C grey; N blue; O red; H omitted. Disordered atoms are omitted for clarity. Hydrogen-bonded interactions shown by blue dotted line.

to inefficient crystallisation rather than formation of other architectures.

In both complexes, the coordination geometry around the silver atoms is substantially distorted from the tetrahedral ideal, as shown by the wide range of bond lengths and angles in Table 2. Most importantly, the twist angle between the two donor sets of each tetrahedron, ideally 90°, is around 79.5° in **3**, and 68° and 71.5° at the two crystallographically independent silver centres in **4**, compensating for the >100° corner piece provided by the ligands.

Both complexes pack in one-dimensional chains of hydrogen-bonded complex cations and counterions (Figure 4). In **3**, these chains propagate parallel to a line bisecting the crystallographic *bc* plane through the origin, with each DDOP alcohol group donating a bifurcated hydrogen bond to one triflate counterion (3.011 Å) and the alcohol group of the next cation (2.886 Å) in the chain. Edge–face contacts of around 3.73 Å suggest a contribution from C–H–π interactions,[20] although there do not appear to be any face–face π–π interactions. In the DDMOP complex **4** the chains run parallel to the crystallographic *a*-axis, with the cations connected by hydrogen bonds between their alcohol groups (2.818 Å), while one of the two triflate anions per formula unit also accepts a hydrogen bond from a DDMOP alcohol group (2.775 Å). The second triflate counterion is disordered and interacts with disordered methanol molecules (2.696 Å), but not the cations. It appears that slipped face-to-face π-stacking interactions may control the association of the hydrogen-bonded chains, with a number of C–C contacts in the range of 3.45–3.92 Å.

Conclusions

A series of closed-shell transition-metal complexes of two novel Schiff-base ligands have been synthesised and charac-

terised in the solid and solution states. These ligands offer two possible coordination modes, and while mononuclear complexes are preferred with cadmium(II), M_2L_2 mesocates form with silver(I). This preference for mononuclear complexes with cadmium(II) prevails over a wide temperature range and is due to the greater ability of Cd^{II} to accept six-coordinate environments, and the consequent gain in stability through formation of two extra coordinate bonds to solvent molecules or counterions. Further investigation will be carried out into the possibility of using the conformational "switch" as a sensor.

Experimental Section

Materials, Methods and Instrumentation: The ligands DDOP and DDMOP were synthesised by reaction of *t*-3,*t*-5-diamino-*r*-1-hydroxycylcohexane with 2-pyridinecarbaldehyde or 6-methyl-2-pyridinecarbaldehyde.[16] All other reagents and solvents were purchased (Fisher/Lancaster/Riedel-de Haën/Aldrich) as AR grade and used without further purification. Deuterated solvents were obtained from Aldrich. All complexations were performed under ambient conditions. IR spectra were measured with a Jasco FTIR-410 spectrometer and ^{1}H NMR measurements were performed at room temperature with Bruker DPX-400 and Avance-400 spectrometers. X-ray diffraction data were collected with a Nonius Kappa-CCD diffractometer with Mo-K_α radiation (λ = 0.7107 Å) and a graphite monochromator.

Preparation of [Cd(DDOP)(NO$_3$)$_2$] (1): DDOP (0.070 g, 0.226 mmol) was dissolved in methanol (20 mL). $Cd(NO_3)_2{\cdot}4H_2O$ (0.105 g, 0.340 mmol) was added in methanol (5 mL) and the solution stirred for 5 h, before the volume was reduced to ca. 3 mL in vacuo. A white solid was removed by filtration and the solution was set for crystallisation by Et_2O diffusion. After 24 h, clear and colourless crystals of **1** were observed (0.030 g, 0.0551 mmol, 23.8% yield). ^{1}H NMR (400 MHz, CD_3OD): δ = 9.01 (d, 2 H, 2Ar*H*), 8.81 [m (s with satellites from coupling to I = 1/2 Cd isotopes ^{111}Cd and ^{113}Cd, combined abundance 25%), 2 H, 2 *H*C=N], 8.33 (pseudo-td, 2 H, 2 Ar*H*), 8.03 (d, 2 H, 2 Ar*H*), 7.94 (m, 2 H, 2 Ar*H*), 4.51 (m, 2 H, 2 *H*C–N), 4.39 (tt, 1 H, *H*COH), 2.34–2.14 (m, 4 H, 3 H_{eq}CH, H_{ax}CH), 2.01 (pseudo-td, 2 H, 2 H_{ax}CH) ppm. IR (KBr disc): $\tilde{\nu}$ = 3431 s, 3062 w, 2933 m, 1651 m, 1595 s, 1423 s, 1296 vs cm^{-1}. $C_{18}H_{20}CdN_6O_7$ (544.80): calcd. C 39.68, H 3.70, N 15.43; found C 39.39, H 3.72, N 15.18.

Preparation of [Cd(DDMOP)(Cl)$_2$]·MeOH (2): DDMOP (0.070 g, 0.208 mmol) was dissolved in methanol (20 mL). $CdCl_2{\cdot}2.5H_2O$ (0.047 g, 0.210 mmol) was added in methanol (5 mL), and the solution stirred overnight, before the volume was reduced to ca 4.5 mL in vacuo. A white solid was removed by filtration and after 24 h, clear, colourless crystals of **2** were produced by diffusion of diethyl ether into the methanolic solution (0.027 g, 0.0489 mmol, 23.5% yield). ^{1}H NMR (400 MHz, CD_3OD): δ = 8.73 [m (s with satellites from coupling to 25% abundace I = 1/2 Cd isotopes), 2 H, 2 *H*C=N], 8.08 (pseudo-t, 2 H, 2 Ar*H*), 7.74 (d, 2 H, 2 Ar*H*), 7.67 (d, 2 H, 2 Ar*H*), 4.68 (tt, 1 H, *H*COH), 4.44 (m, 2 H, 2 *H*CN), 3.03 (s, 6 H, 2 H_3CAr), 2.36–2.13 (m, 4 H, 3 H_{eq}CH, H_{ax}CH), 1.98 (pseudo-td, 2 H, 2 H_{ax}CH) ppm. IR (KBr disc): $\tilde{\nu}$ = 3404 s, 2923 m, 1647 s, 1591 s, 1458 s, 1256 m, 1163 m, 1129 m 1002 m, 808 s cm^{-1}. $C_{21}H_{28}CdCl_2N_4O_2$ (551.79): calcd. C 45.71, H 5.11, N 10.15; found C 45.40, H 4.74, N 10.09.

Preparation of [{Ag(DDOP)}$_2$](CF$_3$SO$_3$)$_2$ (3): DDOP (0.070 g, 0.226 mmol) was dissolved in methanol (20 mL). AgOTf (0.0875 g, 0.339 mmol) was added in methanol (5 mL) and the solution stirred in the dark for 48 h, before the volume was reduced to ca 4 mL in vacuo. After a few minutes, the formation of very small crystals was observed. The solution was filtered and set to crystallise by Et_2O diffusion. Within 24 h, small, colourless cubic or rectangular crystals of **3** were observed (0.0411 g, 0.0364 mmol, 16.1% yield). ^{1}H NMR (400 MHz, CD_3OD): δ = 8.91 (s, 4 H, 4 *H*C=N), 8.39 (d, 4 H, 4 Ar*H*), 8.16 (pseudo-td, 4 H, 4 Ar*H*), 7.92 (d, 4 H, 4 Ar*H*), 7.17 (m, 4 H, 4 Ar*H*), 4.45 (m, 4 H, 4 *H*CN), 4.29 (m, 2 H, 2 *H*COH), 2.13 (m, 8 H, 6 H_{eq}CH, 2 H_{ax}CH), 1.84 (m, 4 H, 4 H_{ax}CH) ppm. IR (KBr disc): $\tilde{\nu}$ = 3429 s, 2924 m, 1645 m, 1593 s, 1441 m, 1281 vs, 1255 vs, 1555 s, 1030 s cm^{-1}. $C_{38}H_{40}Ag_2F_6N_8O_8S_2$ (1130.63): calcd. C 40.37, H 3.57, N 9.91; found C 40.29, H 3.40, N 9.79.

[{Ag(DDMOP)}$_2$](CF$_3$SO$_3$)$_2$·0.5MeOH (4): DDMOP (0.070 g, 0.208 mmol) was dissolved in methanol (20 mL). AgOTf (0.0802 g, 0.310 mmol) was added in methanol (5 mL) and the solution stirred in the dark for 48 h, before the volume was reduced to ca 3 mL in vacuo. After a few minutes, the formation of very small crystals was observed. The solution was filtered and set to crystal-

Table 3. Crystallographic data for **1**–**4**.[a]

	1	**2**	**3**	**4**
Empirical formula	$C_{18}H_{20}CdN_6O_7$	$C_{21}H_{28}CdCl_2N_4O_2$	$C_{38}H_{40}Ag_2F_6N_8O_8S_2$	$C_{42.5}H_{48}Ag_2F_6N_8O_{8.5}S_2$
F_w	544.80	551.77	1130.63	1200.75
Crystal system	monoclinic	triclinic	triclinic	triclinic
a [Å]	12.1888(4)	8.9466(3)	9.0415(7)	12.2018(3)
b [Å]	11.9874(4)	9.3958(3)	11.3901(7)	15.6356(5)
c [Å]	14.0365(5)	14.0929(5)	12.2172(8)	15.8170(5)
α [°]	90	76.769(2)	95.435(4)	61.247(1)
β [°]	91.604(2)	85.356(2)	93.135(3)	70.358(2)
γ [°]	90	76.842(2)	110.024(3)	87.980(2)
Space group	*Pc*	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$
V [Å^3]	2050.10(12)	1122.41(7)	1171.68(14)	2462.21(13)
Z	4	2	1	2
$\rho_{calcd.}$ [g cm^{-3}]	1.765	1.633	1.602	1.620
μ [mm^{-1}]	1.121	1.236	1.005	0.962
T [K]	150(2)	150(2)	293(2)	150(2)
No. observations	20922 (3815 unique)	21739 (4400 unique)	22306 (6684 unique)	37421 (9610 unique)
Residuals R, R_w	0.0624, 0.1634	0.0294, 0.0698	0.0750, 0.2047	0.0659, 0.1722

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

lise by Et_2O diffusion. Within 24 h, small, colourless cubic or rectangular crystals of **4** were observed (0.0744 g, 0.0620 mmol, 59.5% yield). ^{1}H NMR (400 MHz, CD_3OD): δ = 8.90 (d, 4 H, 4 *H*C=N, d due to coupling with I = 1/2 Ag), 8.03 (pseudo-t, 4 H, 4 Ar*H*), 7.74 (d, 4 H, 4 Ar*H*), 7.58 (d, 4 H, 4 Ar*H*), 4.48 (m, 4 H, 4 *H*CN), 4.32 (m, 2 H, 2 *H*COH), 2.26–2.01 (m, 8 H, 6 H_{eq}CH, 2 H_{ax}CH), 2.20 (s, 12 H, 4 H_3CAr), 1.90 (m, 4 H, 4 H_{ax}CH) ppm. IR (KBr disc): $\tilde{\nu}$ = 3423 s, 2920 m, 1642 m, 1592 s, 1458 m, 1278 vs, 1261 vs, 1030 s cm^{-1}. $C_{42}H_{48}Ag_2F_6N_8O_8S_2$ (1186.74, losing solvent): calcd. C 42.58, H 3.91, N 9.46; found C 42.51, H 4.01, N 9.27.

Single-Crystal Structure Determination: Suitable single crystals of **1**–**4** were mounted on the end of a thin glass fibre using Fomblin oil. X-ray diffraction intensity data were measured at 150 or 293 K with a Nonius Kappa-CCD diffractometer [λ(Mo-K_α) = 0.7107 Å]. Structure solution and refinement for **1**–**4** were carried out with SHELXS-97[21] and SHELXL-97[22] using WinGX.[23] Corrections for incident and diffracted beam absorption effects were applied using empirical[24] or numerical methods.[25] Compound **1** crystallised in the space group *Pc* and compounds **2**, **3** and **4** in $P\bar{1}$, as determined by systematic absences in the intensity data, intensity statistics and the successful solution and refinement of the structures. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. Crystal data, data collection parameters and refinement statistics for **1**–**4** are listed in Table 3. CCDC-605439 to -605442 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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