ORIGINAL ARTICLE



Synthesis and characterization of Co(II) and Mn(II) [M₃L₃] triangles

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Abstract

We report an improved method to make the ligand N,N'-(pyrazine-2,5-diylbis(methanylylidene))bis(2-(pyridin-2-yl)ethanamine) (**L**) and the subsequent complexation of this ligand to make the triangular metallo-macrocycles $[Co_3L_3](ClO_4)_6$ ·2H₂O (**C1**·2H₂O) and $[Mn_3L_3](ClO_4)_6$ ·3H₂O (**C2**·3H₂O). Single crystal X-ray analysis of both trimeric circular helicates reveal the complexes pack in enantiomeric pairs in close synergy with the accompanying anions.

Graphical abstract



Keywords Cyclohelicates · Cobalt · Manganese · Pyrazine · Metallo-macrocycle

A contribution in celebration of my friend and collaborator Karsten Gloe on the occasion of his 70th birthday.

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Introduction

The combination of metal ion and ligand allows complexes to self-assemble into a variety of supramolecular architectures. An interesting structure produced by this strategy is the class of cyclohelicates with an $[M_xL_x]$ composition. In these structures each ligand provides two polydentate chelating pockets typically in a bis-bidentate or bis-tridentate fashion, acting as a rigid arm connecting two metal centres [1-5]. The outcome of the self-assembly process is dominated by the design of the bridging ligand and the often-predictable coordination geometry of the metal ion [3, 6]. Due to the wide structural diversity of ligands, and the different metal geometries, it is possible to create cyclohelicates of various shapes including, but not limited to, triangles $[M_3L_3]$ and squares $[M_4L_4]$, the latter being an example of a chiral 2×2 grid complex (Fig. 1) [4, 6].

Ligands composed of two antiparallel bi- or tridentate chelating arms should be designed such that they match the typical binding geometry of the metal [1, 2]. Cyclohelicates containing octahedrally coordinated metal centres are more commonly explored as they have displayed more exotic electrochemical properties, while tetrahedrally coordinated metal centres tend to alter their coordination geometry upon redox processes and are thus less studied [7]. The formation of cyclohelicates can be understood by looking at the directional bonding approach and the molecular library model [8, 9]. The self-assembly of octahedral metal centres with rigid linear bridging ligands is expected to produce a square architecture, however the formation of triangles has been reported [3, 5, 10]. As both square and triangular cyclohelicates can be synthesised under identical conditions, both entropic and enthalpic factors determine which structures will be formed. Entropy favours the formation of the cyclohelicate triangles as more discrete molecules will be formed compared to the cyclohelicate square, however, cyclohelicate squares are more enthalpically favoured due to a lower geometric



Fig.1 An M_4L_4 cyclohelicate $({\bf a})$ and an M_3L_3 cyclohelicate $({\bf b})$ where blue cylinders represent ligands and red spheres represent metal centres

strain [3]. Although the formation of cyclohelicate squares has been reported more frequently, bridging ligands with increased flexibility have been reported to more easily form triangles by distributing geometric strain as smaller deformations throughout the ligand backbone [3, 10].

Pyrazine-based ligands incorporating hydrazone- and amide-type bridges to attach ancillary pyridyl groups have been used extensively in the past to produce M_4L_4 cyclohelicate squares [2, 11, 12]. Previous work by Plieger et al. has also demonstrated the use of iminopyridyl moieties attached to a 3,6-disubstituted pyridazine for the binding of octahedral metal centres [13]. This work incorporates imine-type bridges to produce a pyrazine-based bis-tridentate ligand with two antiparallel N_3 binding environments, which were found to form isomorphic M_3L_3 cyclohelicate triangles with manganese and cobalt.

Results and discussion

Synthesis

A simple 3-step approach (see Scheme 1) has been employed in the synthesis of N, N'-(pyrazine-2,5diylbis(methanylylidene))bis(2-(pyridin-2-yl)ethanamine) (L). 2,5-distyrylpyrazine (2) was synthesized in high purity and good yield by a microwave-mediated condensation based on a report by Coufal et al. [14]. The distyryl derivative was sufficiently pure to use directly in the subsequent ozonolysis to give the aldehyde building block (3) [15]. Following work-up, the ozonolysis product (3) was obtained in sufficient purity, as evidenced by NMR and MS, to be used



Scheme 1 Synthesis of the bis-tridentate ligand L



Fig. 2 X-ray structure of the ligand L

in the final reaction without further purification. Previously, complexations were performed as a one-pot reaction with the Schiff base condensation, however we favour the isolation and characterization of the Schiff base ligand (L) prior to complexation (Fig. 2).

By adopting a microwave based synthesis of the distyryl derivative (2), a reduction in the reaction time to 6 h was achieved with higher purity than that previously reported. The total synthesis was completed in 3 days with an overall yield of 62%. This compares favourably to previously reported methods with, for example the 3 day reaction of Brooker et al. providing L in 54% yield [3]. Our method also provided a more accessible 2-step synthesis of the dicarbaldehyde derivative (3) from 2,5-dimethylpyrazine (1). White needle-like single crystals of the Schiff base ligand (L) suitable for X-ray structural analysis were obtained by hot recrystallization from acetonitrile and confirmed the successful synthesis. The ligand crystalizes in the $P2_1/c$ space group, thus the full ligand structure (Fig. 2) was generated through an inversion centre in the middle of the pyrazine ring. The imine groups adopted an E-conformation and sit in the plane of the pyrazine ring, with the terminal pyridyl groups sitting approximately parallel but displaced above and below the central pyrazine ring.

The complexes $[Co_3L_3](ClO_4)_6$ (**CI**) and $[Mn_3L_3]$ (ClO₄)₆ (**C2**) were synthesised by reacting the preformed ligand, *N*,*N'*-(pyrazine-2,5-diylbis(methanylylidene))bis(2-(pyridin-2-yl) ethanamine), (**L**), with that of the appropriate metal perchlorate salt in acetonitrile. (*Caution: perchlorate salts are potentially explosive and should be handled with appropriate care.*) Upon reduction of volume, crystals were observed to form directly from the reaction mixture. These could be further purified by filtering, dissolving in acetonitrile and subsequently diffusing diethyl ether into the solution containing the respective complex resulted in orange crystals for the Co(II) complex, and dark red crystals for the Mn(II) complex. Initial single crystal X-ray studies on our in-house system provided connectivity and confirmed that the structures were triangular cyclohelicates, analogous to those reported by Brooker et al. [15]. Improved data sufficient to identify the heavily disordered anions was subsequently obtained from the Australian synchrotron facility.

The CHN elemental analyses indicate the presence of six and eight non-coordinated water molecules in C1 and C2, respectively. Samples of each complex were crushed and analyzed by thermogravimetric analysis (TGA) to further confirm the presence of these water molecules. A 5.6% loss in mass was observed for C1 over 4 h, corresponding to the loss of 6 water molecules. C2 was observed to decrease in mass by 7.2% over 2.5 h, corresponding to the loss of almost 8 water molecules, followed by an energetic event causing an instantaneous 8% decrease in total mass indicating sample removal off the thermobalance. These results are consistent with the presence of water observed in the X-ray crystal structure determinations. Conductivity studies indicated both C1 and C2 have high electrolyte cation to anion ratios, however, due to the low mobility in solution and low solubilities of the complexes no reliable conclusions about exact electrolyte ratios can be drawn.

Each complex is isomorphic with each other and with the previously reported $[Zn_3L_3](BF_4)_6$ of Brooker et al. [3]. The asymmetric unit contains a ML fragment which comprises one-third of the complex, and two perchlorate anions disordered over five sites. Applying the symmetry operation (3-fold rotation through the centre of the triangle of the complex for $R\bar{3}c$) perpendicular to the M₃ plane, results in the generation of the full triangular metallo-macrocycle (Fig. 3).

Each octahedral coordinated metal cation shares an N_3 donor set from two different ligands comprising pyrazine, imine and pyridine donor nitrogen atoms. The bond lengths for the metals are consistent with the (+2) oxidation state for



Fig. 3 X-ray structure of the cation $[Mn_3L_3]^{6+}$

each cation. Selected bond distances and angles are shown in Table 1.

Overall, the structure of each metallo-macrocycle is chiral, with both enantiomers contained within the $R\bar{3}c$ crystal symmetry.

The improved quality of the reflection data for both of these structures allowed the positions of the anions to be clearly identified. Each enantiomeric cation is balanced by six perchlorate anions. One ClO_4^- lies on the six-fold centre of symmetry with one Cl–O bond aligned with the three-fold rotation axis in the centre of the triangle. It is therefore 'pointing' towards one enantiomer half the time and towards the other enantiomer the other half of the time (Fig. 4).

A second perchlorate anion occupies the mirror position on the other side of each enantiomer, again with a Cl–O bond aligned along the three-fold rotation axis. As such, the packing can be considered as pairs of enantiomers with one shared perchlorate anion between them. The remaining perchlorate anions are distributed in the naturally occurring voids this structure provides. One fully occupied perchlorate sits above, but skewed towards one of the nitrogen donors on the pyrazine ring on each face of the metallo-macrocyclic triangle. It also sits in close proximity to one of the two terminal pyridine rings. The remaining 1.5 perchlorates are distributed evenly around the outer face of the triangle (0.5 occupancy per side) again sitting above and now towards the other pyrazine nitrogen donor. These again interact weakly with the other terminal pyridine ring on each side of the triangle (Fig. 5).

As all examples to date have utilised similar sized anions $(BF_4^- vs. ClO_4^-)$ in the structural determinations, it remains to be seen whether a difference in incorporated anion will have any influence on the overall structure of these triangular metallo-macrocycles.

Table 1 Selected bond lengths and angles for the C1·2H₂O and C2·3H₂O

C1·2H ₂ O		C2·3H ₂ O		
Bond lengths	Å	Bond lengths	Å	
Co-N1 ¹ _{pyz}	2.200 (3)	$Mn-N1^{1}_{pvz}$	2.343 (2)	
Co-N2 _{pyz}	2.216 (3)	Mn–N2 _{pvz}	2.341 (2)	
Co-N4 _{imine}	2.162 (3)	Mn–N4 _{imine}	2.217 (2)	
Co-N0AA ¹ _{imine}	2.142 (3)	Mn–N0AA ¹ _{imine}	2.218 (2)	
Co-N6 _{pvrid}	2.133 (3)	Mn–N6 _{pyrid}	2.203 (2)	
Co-N5B ¹ _{pyrid}	2.08 (2)	Mn–N5B ¹ _{pvrid}	2.11 (2)	
Co-N5 ¹ _{pyrid}	2.207 (3)	$Mn-N5^{1}_{pyrid}$	2.267 (18)	
Bond angles	Angle/°	Bond angles	Angle/°	
N1 ¹ -Co-N2	81.64 (10)	N1 ¹ –Mn–N2	81.04 (6)	
N1 ¹ -Co-N5 ¹	159.1 (5)	$N1^{1}$ -Mn- $N5^{1}$	157.00 (6)	
N0AA ¹ -Co-N1 ¹	76.07 (11)	N0AA ¹ -Mn-N1 ¹	71.96 (6)	
N0AA ¹ -Co-N2	90.19 (12)	N0AA ¹ -Mn-N2	87.16 (6)	
N0AA ¹ -Co-N4	163.68 (12)	N0AA ¹ -Mn-N4	155.51(7)	
N0AA ¹ -Co-N5 ¹	83.5 (4)	N0AA ¹ -Mn-N5 ¹	85.2 (5)	
N6-Co-N1 ¹	86.30 (11)	N6–Mn–N1 ¹	84.77 (6)	
N6C0N2	159.81 (11)	N6-Mn-N2	155.79 (6)	
N6–Co–N0AA ¹	102.59 (12)	N6-Mn-N0AA ¹	106.97 (7)	
N6-Co-N4	88.73 (12)	N6-Mn-N4	87.69 (7)	
N6–Co–N5 ¹	102.6 (7)	N6–Mn–N5 ¹	104.7 (6)	
N4–Co–N1 ¹	93.20 (12)	N4–Mn–N1 ¹	90.51 (7)	
N4-Co-N2	75.92 (12)	N4–Mn–N2	72.99 (7)	
N4–Co–N5 ¹	105.7 (4)	N4–Mn–N5 ¹	110.4 (5)	
N5B ¹ -Co-N1 ¹	168.1 (5)	N5B ¹ -Mn-N1 ¹	163.4 (5)	
N5B ¹ –Co–N2	92.9 (7)	N5B ¹ -Mn-N2	96.6 (8)	
N5B ¹ -Co-N0AA ¹	93.5 (4)	N5B ¹ -Mn-N0AA ¹	91.5 (5)	
N5B ¹ -Co-N6	101.7 (7)	N5B ¹ -Mn-N6	102.4 (7)	
N5B ¹ -Co-N4	95.7 (4)	N5B ¹ -Mn-N4	104.6 (6)	
N5 ¹ -Co-N2	94.3 (7)	N5 ¹ -Mn-N2	95.8 (6)	

 $^{1}1 - Y, +X - Y, +Z$



Fig. 4 A pair of enantiomeric helicates showing the centrally shared perchlorate positionally disordered over two sites



Fig. 5 Space filling enantiomeric pair showing the flanking perchlorates sitting on the outside face of the trimeric helicates

Conclusion

There are now four crystallographic examples of this ligand with differing octahedral coordination capable transition metals and in every case the metallo-macrocycle generated is one of a M_3L_3 variation as opposed to other stoichiometries, for example that of the analogous diamide ligand [15]. Based on the available evidence it is clearly a ligandbased phenomena due primarily to the flexibility that this particular ligand possesses. A study on whether a change in the incorporated anion would influence structure is nonetheless worthwhile and both this and electrochemical investigations are on-going.

Materials and analysis

All reagents were obtained from commercial sources and used without further purification. Commercially sourced HPLC grade acetonitrile and methanol was dried over activated 3 Å molecular sieves for at least 1 week prior to use. Microwave synthesis was performed using a CEM Discovery Monomode Explorer operating at 100 Watts. Ozonolysis was performed using a CD10/AD Corona Discharge Ozone Generator. The synthesized ligand and precursors were characterized by ¹H and ¹³C NMR spectroscopy (solutions in DMSO-d₆ or CDCl₃, at room temperature) using a Bruker Avance 500 MHz spectrometer. Melting points were recorded on a Gallenkamp melting point apparatus, and are uncorrected. High resolution mass spectrometry was performed using a ThermoScientific O Exactive Focus Hybrid Quadrupole-Orbitrap Mass Spectrometer. Thermogravimetric analysis (TGA) was performed on a Q50 TGA apparatus. The Campbell Microanalytical Laboratory, University of Otago, provided CHN elemental analysis. UV-Vis spectra were collected on a Shimadzu UV-3101PC spectrophotometer. Conductivity measurements were performed with a Philips PW9509 conductivity meter.

Synthesis of 2,5-distyrylpyrazine (2)

2,5-Dimethylpyrazine (0.99 g, 9.15 mmol), benzaldehyde (4.00 mL, 39.4 mmol) and benzoic anhydride (4.97 g, 22.0 mmol) were stirred in a microwave tube until full dissolution occurred. Argon was bubbled through the yellow mixture and was reacted at 175 °C in the microwave for 5 h, with rapid stirring. After cooling, a dark brown solid was obtained, which was suspended in cold ethanol before filtering and washing with cold ethanol to yield a yellow crystalline solid (1.61 g, 5.7 mmol, 62%). This product was carried through to the next reaction without further purification. ¹H NMR (500 MHz, CDCl₃): δ 8.60 (2H, s, ArH), 7.74 (2H, d, J = 16 Hz, CH), 7.63–7.59 (4H, m, ArH), 7.43–7.31 (6H, m, ArH), 7.19 (2H, d, J = 16 Hz, CH).

Synthesis of pyrazine-2,5-dicarbaldehyde (3)

The dicarbaldehyde derivative was prepared as previously reported by Brooker et al. [15]. ¹H NMR data corresponds to literature values.

Synthesis of *N,N'*-(pyrazine-2,5-diylbis(methanylyli dene))bis(2-(pyridin-2-yl)ethanamine) (L)

2-(2-Aminoethyl)pyridine (1.02 g, 3.0 mmol) was added to a stirred solution of pyrazine-2,5-dicarbaldehyde (0.52 g, 1.5 mmol) in 10 mL acetonitrile. The mixture was stirred at room temperature for 30 min then left to stand in a freezer at -5 °C for 3 h. The precipitated solid was filtered and washed with cold acetonitrile to yield **L** as a white crystalline solid (0.32 g, 0.9 mmol, 62%). Recrystallization from hot acetonitrile yielded white crystals of X-ray quality. ¹H NMR (500 MHz, DMSO-d₆): δ 9.14 (2 H, s, HC=N), 8.55 (2 H, d, J=4.10 Hz, pyH), 8.35 (2 H, t, J=1.27 Hz, pzH), 7.58 (2 H, td, J=1.57, 7.6 Hz, pyH), 7.18 (2 H, d, J=7.87 Hz, pyH), 7.12 (2 H, ddd, J=0.99, 4.94, 7.44 Hz, pyH), 4.13 (4 H, dt, J=7.26, 1.26 Hz, CH₂), 3.24 (4 H, t, J=7.1 Hz, CH₂). MS: m/z=345 (M⁺, 100%). UV/Vis λ_{max} (MeCN) 257 nm (21000 L mol⁻¹ cm⁻¹), 291 nm (22019 L mol⁻¹ cm⁻¹). MP 138 °C (Sample decomposed at this temperature).

Synthesis of $[Co_3L_3](ClO_4)_6 \cdot 6H_2O(C1 \cdot 6H_2O)$

A solution of Co(ClO₄)₂·6H₂O (0.14 g, 0.39 mmol) in 3 mL acetonitrile was added to a solution of L (0.13 g, 0.39 mmol) in 30 mL acetonitrile producing a orange solution. The mixture was stirred for 30 min then concentrated in vacuo to give orange crystals. Vapour diffusion of diethyl ether into a concentrated solution of $[Co_3L](ClO_4)_6$ in acetonitrile yielded more orange crystalline material. The product was filtered then recrystallized by vapour diffusion of diethyl ether into a concentrated solution of $[Co_3L_3](ClO_4)_6$ in acetonitrile to yield orange crystals of X-ray quality (0.10 g, 0.13 mmol, 39%). Elemental analysis calcd for [Co₃L₃](ClO₄)₆·6H₂O: C 37.63, H 3.79, N 13.17%. Found: C 37.69, H 3.34, N 13.02%. UV/Vis λ_{max} (MeCN) 240 nm (50195 L mol⁻¹ cm⁻¹), 326 nm (33512 $L \text{ mol}^{-1} \text{ cm}^{-1}$), 406 nm (8305 $L \text{ mol}^{-1} \text{ cm}^{-1}$). Conductivity of $[Co_3L_3](ClO_4)_6$ in CH₃CN=0.416 mS cm⁻¹, 419.01 S cm² mol^{-1} .

Synthesis of $[Mn_3L_3](CIO_4)_6 \cdot 8H_2O(C2 \cdot 8H_2O)$

A solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.13 g, 0.35 mmol) in 10 mL acetonitrile was added to a solution of L (0.12 g, 0.35 mmol) in 20 mL acetonitrile producing a dark red coloured solution. The mixture was stirred for 30 min then concentrated *in vacuo*. Vapour diffusion of diethyl ether into a concentrated solution of $[Mn_3L_3](ClO_4)_6$ in acetonitrile yielded dark red crystals of X-ray quality (0.03 g, 0.12 mmol, 15%). Elemental analysis calcd for $[Mn_3L_3](ClO_4)_6 \cdot 8H_2O: C 37.17, H 3.95, N 13.00\%$. Found: C 37.59, H 3.58, N 13.25%. UV/Vis λ_{max} (MeCN) 248 nm (41565 L mol⁻¹ cm⁻¹), 306 nm (38730 L mol⁻¹ cm⁻¹), 400 nm (weakly absorbing shoulder). Conductivity of $[Mn_3L_3]$ (ClO₄)₆ in CH₃CN=0.320 mS cm⁻¹, 554.76 S cm⁻² mol⁻¹.

The characteristic FTIR bands (cm⁻¹) of ligand L and complexes C1 and C2

N,*N*'-(pyrazine-2,5-diylbis(methanylylidene))bis(2-(pyridin-2-yl)ethanamine) (**L**): 1642 (m), 1590 (m), 1571 (m), 1477

(w), 1437 (m), 1379 (w), 1348 (w), 1327 (w), 1121 (s), 1086 (s), 1035 (s).

 $\label{eq:constraint} \begin{array}{l} [Co_3L_3](ClO_4)_6 \ (\textbf{C1}): \ 1631 \ (w), \ 1608 \ (m), \ 1571 \ (w), \\ 1484 \ (w), \ 1446 \ (m), \ 1402 \ (w), \ 1363 \ (w), \ 1317 \ (m), \ 1307 \\ (m), \ 1251 \ (w), \ 1191 \ (m), \ 1165 \ (w), \ 1019 \ (m), \ 985 \ (w), \ 952 \\ (m), \ 882 \ (w), \ 864 \ (w), \ 840 \ (w), \ 831 \ (w), \ 825 \ (w), \ 813 \ (w), \\ 784 \ (w), \ 768 \ (m), \ 755 \ (m), \ 741 \ (m), \ 724 \ (m), \ 717 \ (m), \ 699 \\ (w), \ 684 \ (w). \end{array}$

 $[Mn_{3}L_{3}](ClO_{4})_{6} (C2): 1641 (w), 1608 (m), 1486 (w), 1443 (m), 1403 (w), 1311 (m), 1183 (m), 1017 (m), 959 (m), 844 (m), 768 (m).$

X-ray crystallography

Single crystal diffraction data for ligand L was collected at 120 K on an Agilent SuperNova diffractometer (using focused microsource Cu K α radiation, $\lambda = 1.54184$ Å) with an EOS S2 detector. The structures were solved by direct methods SHELXS and refined using the SHELXL as implemented in the Olex2 software package [16–18]. Absorption data scaling corrections were carried out using multiscan. Hydrogens were calculated at their ideal positions unless otherwise stated. Single crystal diffraction data for complexes C1 and C2 was collected at 110 K on the MX2 beamline ($\lambda = 0.7093$ Å) at the Australian Synchrotron, Victoria, Australia. The dataset was processed and evaluated using XDS [19]. The resulting reflections were scaled using AIMLESS140 from the CCP4 program suite [20]. The structures were solved by direct methods SHELXS and refined using the SHELXL as implemented in the Olex2 software package [16-18]. Absorption data scaling corrections were carried out using multiscan. All non-H atoms were refined with anisotropic thermal parameters. All H atoms were inserted at calculated positions and rode on the C atoms to which they were attached. TwinRotMat indicated the presence of a non-merohedral twin law $(-1\ 0\ 0,\ 0\ -1\ 0,\ 0.666\ 0\ 1)$ which was duly applied to the data for L, resulting in 2% improvement in R_1 , BASF = 10.8%. Positional disorder was present in both complexes. In both cases, one of the pyridine arms is positional disordered in a 50:50 ratio. In addition, one of the perchlorate anions is rotational disordered in a 45:55 ratio (C1), and 47:53 (C2). In both structures, one of the cavities is shared by one perchlorate anion 50% of the time and residue water solvent over two (C1) and four (C2) sites. Remaining diffuse solvent in C1 and C2 was treated with SQUEEZE [21] as implemented in the Olex2 software package. A total of 674 and 873 electrons were removed per unit volume (or 56 and 73 electrons per asymmetric unit) for the complexes C1 and C2 respectively. These approximated to 1.333 molecules of water and two molecules of CH₃CN per asymmetric unit for C1 with Z = 12

Table 2	Crystallographic	data and	structure refinement	details for a	all compounds
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	L	C1	C2
CCDC number	1890125	1890162	1890780
Empirical formula	$C_{20}H_{20}N_{6}$	$C_{60}H_{60}Cl_6Co_3N_{18}O_{26}$	$C_{60}H_{66}Cl_6Mn_3N_{18}O_{27}$
Formula weight	344.42	1838.76	1848.82
T/K	120(1)	100(2)	100(2)
Crystal system	monoclinic	trigonal	trigonal
Space group	P2 ₁ /c	R3c	R3c
a/Å	6.0968(2)	25.397(4)	25.397(4)
b/Å	4.60769(17)	25.397(4)	25.397(4)
c/Å	31.7665(12)	45.748(9)	45.748(9)
β/°	93.622(3)	90	90
γ/°	90	120	120
Volume/Å ³	890.61(6)	25554(9)	25554(9)
Z	2	12	12
$\rho_{calc}g/cm^3$	1.284	1.434	1.442
μ/mm^{-1}	0.640	0.846	0.709
F(000)	364	11244	11340
Crystal size/mm ³	$0.149 \times 0.136 \times 0.046$	$0.02 \times 0.005 \times 0.003$	$0.15 \times 0.12 \times 0.1$
Radiation	Cu Ka ($\lambda = 1.54184$)	Mo Ka ($\lambda = 0.71073$)	Mo Ka ($\lambda = 0.71073$)
2Θ range for data collection/°	8.366 to 145.99	4.98 to 52.598	2.568 to 56.61
Index ranges	$-4 \le h \le 7, -5 \le k \le 5, -39 \le l \le 39$	$-31 \le h \le 31, -31 \le k \le 31, -55 \le 1 \le 55$	$-33 \le h \le 33, -33 \le k \le 33, -60 \le 1 \le 60$
Reflections collected	4850	54503	131410
Independent reflections	1708 [R _{int} =0.0284, R _{sigma} =0.0288]	5627 [R _{int} =0.0694, R _{sigma} =0.0381]	7067 [R _{int} =0.0720, R _{sigma} =0.0236]
Data/restraints/parameters	1708/0/119	5627/268/481	7067/312/509
Goodness-of-fit on F ²	1.156	1.049	1.039
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0790, wR_2 = 0.2307$	$R_1 = 0.0660, wR_2 = 0.2040$	$R_1 = 0.0535, wR_2 = 0.1614$
Final R indexes [all data]	$R_1 = 0.0838, wR_2 = 0.2385$	$R_1 = 0.0765, wR_2 = 0.2177$	$R_1 = 0.0559, wR_2 = 0.1640$
Largest diff. peak/hole/e $Å^{-3}$	0.40/-0.28	0.86/-0.42	0.74/-0.76

(~57 e–) and three molecules of water and two molecules of CH₃CN per asymmetric unit for C2 with Z = 12 (~74 e–). The crystallographic data are summarised in Table 2.

References

- Bark, T., Düggeli, M., Stoeckli-Evans, H., von Zelewsky, A.: Designed molecules for self-assembly: the controlled formation of two chiral self-assembled polynuclear species with predetermined configuration. Angew. Chem. Int. Ed. 40(15), 2848–2851 (2001)
- Hausmann, J., Brooker, S.: Control of molecular architecture by use of the appropriate ligand isomer: a mononuclear "corner-type" versus a tetranuclear [2 × 2] grid-type cobalt(III) complex. Chem. Commun. 13, 1530–1531 (2004)
- Hogue, R.W., Dhers, S., Hellyer, R.M., Luo, J., Hanan, G.S., Larsen, D.S., Garden, A.L., Brooker, S.: Self-assembly of cyclohelicate [M3L3] triangles Over [M4L4] squares, despite nearlinear bis-terdentate L and octahedral M. Chem. Eur. J. 23(57), 14100–14100 (2017)
- Steed, J.W., Atwood, J.L.: Supramolecular chemistry. Wiley, Hoboken (2013)

- Zhang, L., August, D.P., Zhong, J., Whitehead, G.F.S., Vitorica-Yrezabal, I.J., Leigh, D.A.: Molecular trefoil knot from a trimeric circular helicate. J. Am. Chem. Soc. **140**(15), 4982–4985 (2018)
- Greig, L.M., Philp, D.: Applying biological principles to the assembly and selection of synthetic superstructures. Chem. Soc. Rev. 30(5), 287–302 (2001)
- Hanan, G.S., Volkmer, D., Lehn, J.-M.: Coordination arrays—synthesis and characterization of tetranuclear complexes of grid-type. Can. J. Chem. 82(10), 1428–1434 (2004)
- Holliday, B.J., Mirkin, C.A.: Strategies for the construction of supramolecular compounds through coordination chemistry. Angew. Chem. Int. Ed. 40(11), 2022–2043 (2001)
- Leininger, S., Olenyuk, B., Stang, P.J.: Self-assembly of discrete cyclic nanostructures mediated by transition metals. Chem. Rev. 100(3), 853–908 (2000)
- Chakrabarty, R., Mukherjee, P.S., Stang, P.J.: Supramolecular coordination: self-assembly of finite two- and three-dimensional ensembles. Chem. Rev. **111**(11), 6810–6918 (2011)
- Hausmann, J.: Transition Metal complexes of pyrazine based bisterdentate diamide ligands. University of Otago, New Zealand (2004)
- Shen, F., Huang, W., Wu, D., Zheng, Z., Huang, X.-C., Sato, O.: Redox modulation of spin crossover within a cobalt metallogrid. Inorg. Chem. 55(2), 902–908 (2016)

- Plieger, P.G., Downard, A.J., Moubaraki, B., Murray, K.S., Brooker, S.: Dimetallic complexes of acyclic pyridine-armed ligands derived from 3,6-diformylpyridazine. Dalton Trans. 14, 2157–2165 (2004)
- Coufal, R., Prusková, M., Císařová, I., Drahoňovský, D., Vohlídal, J.: Simple and efficient access to pyrazine-2,5- and -2,6-dicarbaldehydes. Synth. Commun. 46(4), 348–354 (2016)
- Brooker, S., Kelly, R.J.: Synthesis and structure of dilead(II) and dimanganese(II) complexes of macrocycles derived from 3,6-diformylpyridazine. J. Chem. Soc. Dalton Trans. 10, 2117– 2122 (1996)
- Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. 42(2), 339–341 (2009)
- Palatinus, L., van der Lee, A.: Symmetry determination following structure solution in P1. J. Appl. Crystallogr. 41(6), 975–984 (2008)
- Sheldrick, G.M.: Crystal structure refinement with SHELXL. Acta Crystallogr. Sect. C. 71, 3–8 (2015)

- 19. Kabsch, W.: XDS. Acta Crystallogr. Sect. D. 66, 125–132 (2010)
- Winn, M.D., Ballard, C.C., Cowtan, K.D., Dodson, E.J., Emsley, P., Evans, P.R., Keegan, R.M., Krissinel, E.B., Leslie, A.G.W., McCoy, A., McNicholas, S.J., Murshudov, G.N., Pannu, N.S., Potterton, E.A., Powell, H.R., Read, R.J., Vagin, A., Wilson, K.S.: Overview of the CCP4 suite and current developments. Acta Crystallogr. Sect. D. 67(4), 235–242 (2011)
- Spek, A.: Platon squeeze: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. Acta Crystallogr. Sect. C. **71**(1), 9–18 (2015)

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