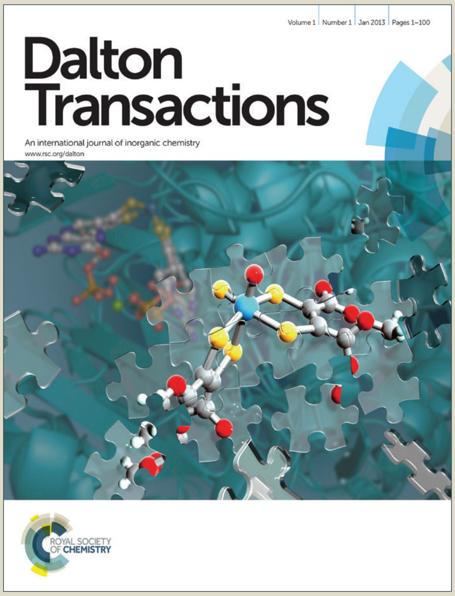
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

New topology of CN-bridged clusters: dodecanuclear face-sharing defective cubes based on octacyanometallates(IV) and nickel(II) with diimine ligands

Beata Nowicka,[*a] Christian Näther,[b] Alexandra Halemba,[a] Mateusz Reczyński,[a] and Barbara Sieklucka[a]

[a]*Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland*

[b]*Institut für Anorganische Chemie, Christian-Albrechts-Universität, Max-Eyth.-Str. 2,*

24118 Kiel, Germany

Abstract

New dodecanuclear bimetallic Ni_8M_4 clusters were obtained in the reaction between octacyanometallates(IV), nickel(II) cations and diimine ligands. $\{[Ni(LL)(H_2O)]_2[Ni(LL)(H_2O)_2]_6[M(CN)_8]_4\}$ assemblies, where LL = 1,10-phenanthroline M = Mo, (**1**) or LL = 2,2'-bipyridine M = W (**2**) or Mo (**3**), are among the largest octacyanometallate-based clusters. They show the same compact topology of the cluster core, which can be described as defective face-sharing cubes with corners defined by alternating metal centres. The structures are stabilised by π-π interactions between aromatic rings of diimine ligands and hydrogen bonds connecting terminal CN groups and coordinated H_2O molecules through crystallisation solvent. Different decorating ligands cause different arrangement of clusters in the crystal structure. **1** crystallises in triclinic system space group P-1, while **2** and **3** in monoclinic system space group $P2_1/n$. The clusters show paramagnetic behaviour with weak antiferromagnetic interactions between the Ni^{II} centres though diamagnetic $NC\text{-}M^{IV}\text{-}CN$ linkages.

Introduction

Cyano-bridged discrete bimetallic assemblies exhibit a range of interesting properties, including single molecule magnet (SMM) behaviour, photomagnetism, spin-crossover (SCO), optical activity and high-spin ground state.[1,2] Thanks to these characteristics they are intensely studied as potential molecular switches and sensors, memory elements or magnetic coolers. They also provide models for theoretical studies, which can be extended to higher dimensionality systems.[3]

Cyano-bridged clusters are constructed by the building-block approach in self-assembly processes in solution. The combination of polycyanometallates and transition metal cations with labile coordination sites leads to the formation of CN-bridged assemblies. The development of extended structures is usually prevented by the use of appropriate blocking ligands on one or both metal centres. The nuclearity and topology of the clusters depends on the relative charges of the ions as well as the number and spatial arrangement of the CN-groups in the anionic building block and labile ligands coordinated to the cations. It varies greatly from the smallest tetranuclear squares to complicated structures containing over twenty metal centres. The simplest topology patterns: square and trigonal bipyramid are common for both hexa- and octa- coordinated cyanometallates.[1,2] They are also encountered in larger clusters in form of decorated or repeated vertex-sharing motives. More complex topologies (Figure 1) often require particular geometry of the bridges and are therefore restricted to certain types of polycyanometallates. For instance cube topology, based on the right angles between facially arranged ligands, can be observed only for octahedral complexes.[4] Face-centred cube structure composed of 14 metal centres is typical for hexa- and tetra-coordinated cyanometallates.[5] Conversely, octacyanometallates with their flexible coordination sphere can form topologies unattainable for hexacyanometallates. One of them is an octahedron formed by two $[M(CN)_8]^{4-}$ anions and four divalent cations. Three isostructural clusters of this type[6] and one related structure of decorated octahedron[7] have been characterised. The most characteristic for octacyanometallates are $M^{II}_9M^{V}_6$ discrete assemblies of the body-centred six-capped cube topology, which surprisingly can be obtained without the use of any blocking ligands.[8] Rich family of $M^{II}_9M^{V}_6$ clusters comprises over 20 structures based on different metal ions with various decorating ligands on the surface.[8-10] Apart from this high-symmetry compact structure large octacyanometallate-based clusters containing over ten metal centres are very rare. There are two isostructural octadecanuclear clusters in the form of decorated rings.[11] The largest 21-centred cluster is a unique intricate construction described as an open winged cage, which comprises octacyanotungstate in two different oxidation states (IV and V) and Cu(II) ions.[12] In this work we report two new dodecanuclear cluster structures of unprecedented topology of defective stacked cubes.

Experimental

Synthesis

$K_4[Mo(CN)_8]\cdot 2H_2O$ and $K_4[W(CN)_8]\cdot 2H_2O$ were synthesized as described in literature.[13] All other chemicals of reagent grade were used as supplied.

$\{[Ni(phen)(H_2O)]_2[Ni(phen)(H_2O)_2]_6[Mo(CN)_8]_4\}\cdot 30H_2O$ (1) A solution of 1,10-phenanthroline·1H_2O (39.6 mg, 0.2 mmol) in MeOH/H_2O (4:1, 10 ml) was added to a solution of $NiCl_2\cdot 6H_2O$ (47.5 mg, 0.2 mmol) in MeOH/H_2O (4:1, 10 ml) with constant stirring. Then this solution was added to a solution of $K_4[Mo(CN)_8]\cdot 2H_2O$ (49.6 mg, 0.1 mmol) in MeOH/H_2O (4:1, 20 ml) with constant stirring. At first green powder precipitated, which after some weeks recrystallized. Resulting green crystals were washed several times by decantation with solvent mixture analogical to mother liquor.

(Found: C, 38.75; H, 3.42; N, 17.45; Calc. for $C_{128}H_{152}N_{48}O_{44}Ni_8Mo_4$: C, 39.22; H, 3.91; N, 17.15.) IR ν(C≡N): 2115.5s, 2147.8m cm^{-1}.

$\{[Ni(bpy)(H_2O)]_2[Ni(bpy)(H_2O)_2]_6[W(CN)_8]_4\}\cdot 24H_2O$ (2) A solution of 2,2‘-bipyridine (31.2 mg, 0.2 mmol) in MeOH/DMF (10:1, 11 ml) was added to a solution of $NiCl_2\cdot 6H_2O$ (47.5 mg, 0.2 mmol) in MeOH/DMF (5:1, 6 ml) with constant stirring. Then this solution was added to a solution of $K_4[W(CN)_8]\cdot 2H_2O$ (58.4 mg, 0.1 mmol) in H_2O/MeOH/DMF (7:1:1, 27 ml) with constant stirring. At first green powder precipitated, which after some weeks recrystallized. Resulting green crystals were washed several times by decantation with solvents mixture analogical to mother liquor.

(Found: C, 33.90; H, 3.50; N, 16.83; Calc. for $C_{112}H_{140}N_{48}O_{38}Ni_8W_4$: C, 33.87; H, 3.55; N, 16.93.) IR ν(C≡N): 2108.8s, 2116.0sh, 2144.9m, 2153.6sh cm^{-1}.

$\{[Ni(bpy)(H_2O)]_2[Ni(bpy)(H_2O)_2]_6[Mo(CN)_8]_4\}\cdot 24H_2O$ (3) A solution of 2,2‘-bipyridine (31.2 mg, 0.2 mmol) in H_2O/MeOH/MeCN (10:2:1, 6.5 ml) was added to a solution of $NiCl_2\cdot 6H_2O$ (47.5 mg, 0.2 mmol) in H_2O/MeOH/MeCN (10:2:1, 6.5 ml) with constant stirring. Then this solution was added to a solution of $K_4[Mo(CN)_8]\cdot 2H_2O$ (49.6 mg, 0.1 mmol) in H_2O/MeOH/MeCN (8:4:1, 6.5 ml) with constant stirring. At first green powder precipitated, which after some weeks recrystallized. Resulting green crystals were washed several times by decantation with solvents mixture analogical to mother liquor.

(Found: C, 36.69; H, 4.31; N, 18.35; calc. for $C_{112}H_{140}N_{48}O_{38}Ni_8Mo_4$: C, 37.16; H, 3.90; N, 18.57.) IR ν(C≡N): 2112.2s, 2151.2m, 2161.3sh cm^{-1}.

Structure determination

X-ray diffraction measurements were performed using an Imaging Plate Diffraction System IPDS-2 from STOE & CIE with MoK_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[14] and refinement was performed against F^2 using SHELXL-2013.[15] A numerical absorption correction was performed ($T_{min/max}$: 0.7728/0.8986 for **1** and 0.4894/0.6093 for **2**). All non H atoms were refined anisotropic. The C-H H atoms were positioned with idealized geometry and were refined isotropic with $U_{iso}(H) = 1.2\ U_{eq}(C)$ (1.5 for methyl H atoms) using a riding model. For some of the water molecules the H atoms were located, their bond lengths set to ideal values and finally they were refined isotropic with $U_{iso}(H) = 1.5\ U_{eq}(O)$ using a riding model. However, all O-H H atoms were considered in the calculation of the molecular weights. In both compounds some positions were occupied by coordinating water and methanol molecules and were refined using a split model. In **1** a methyl group of a methanol molecule is disordered in two positions and was refined using a split model using restraints. Some of the positions of the non-coordinating water molecules are not fully occupied. After refinement of all atoms there was still some residual electron density in cavities of the structure indicating the presence of additional disordered solvent molecules. Therefore, the data were corrected for disordered solvent using the SQUEEZE option in Platon.[16] Graphics were created with Mercury 3.3.[17]

Measurements and calculations

Elemental analyses were performed on an ELEMENTAR Vario Micro Cube CHNS analyzer. Magnetic measurements were performed using a Quantum Design MPMS-3 EVERCOOL magnetometer. Powder XRD patterns for samples in the form of thick suspensions sealed in 0.7 mm glass capillaries were measured on a PANalytical X'Pert PRO MPD diffractometer with a capillary spinning add-on using CuKα radiation (λ = 1.54187 Å). The patterns were collected at room temperature between 3 and 70° 2θ angle. The reference powder patterns were generated using Mercury 3.3 software.[17] IR spectra in 4000–500 cm^{-1} range were measured on a Thermo Scientific Nicolet iS5 spectrometer with iD5 ATR-Diamond add-on. Continuous Shape Measure analysis for the coordination spheres of eight-coordinated M^{IV} centres and six-coordinated Ni^{II} centres was performed using SHAPE software ver. 2.1 available free of charge.[18]

Results and discussion

Synthesis

The reaction between the $[M(CN)_8]^{4-}$ anions (M = Mo, W) and in situ formed complex of Ni^{2+} cations with diimine ligand LL = 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) in 1:1 ratio led to the formation of dodecanuclear CN-bridged clusters of composition: $\{[Ni(phen)(H_2O)]_2[Ni(phen)(H_2O)_2]_6[Mo(CN)_8]_4\}\cdot 30H_2O$ (**1**), $\{[Ni(bpy)(H_2O)]_2[Ni(bpy)(H_2O)_2]_6[W(CN)_8]_4\}\cdot 24H_2O$ (**2**) and $\{[Ni(bpy)(H_2O)]_2[Ni(bpy)(H_2O)_2]_6[Mo(CN)_8]_4\}\cdot 24H_2O$ (**3**). The products crystallise over a few weeks from the initial amorphous precipitate. For **1** and **2** crystals suitable for structure analysis were obtained, while **3** crystallised in the form of small aggregates but it was proved isostructural with **2** by powder XRD (Figure S1). The crystals kept under solvent mixture analogical to mother liquor are stable for several weeks. Dried on air they retain their crystalline form for several hours, then they gradually break and turn into powder after a few days. Single-crystal XRD measurements were performed on crystals freshly taken from solution, covered in grease and quickly cooled to 200 (**1**) or 150 K (**2**). The results of the structure determination for **1** and **2** show the presence of both H_2O and MeOH interchangeably as ligands on the Ni cations. It may be connected with similarity of both O-donating ligands and labile character of Ni complexes. The structures also contain considerable amount of crystallisation solvent, most of which is highly disordered, especially in compound **1**, and therefore it could not be fully located or identified. The elemental analyses of compounds **1**-**3** were performed on samples which after drying were in contact with air for about two weeks and attained the powder form. The formulae derived from the results indicate that in the compounds stable in air only water is present as both coordinated and non-coordinated solvent. The calculated amount of crystallisation water (30 H_2O for **1** and 24 for **2**) is consistent with the total solvent accessible volume calculated by Platon[16] upon removal of all non-coordinated solvent molecules and replacement of coordinated MeOH by H_2O in both structures (1147 and 904 $Å^3$ per formula unit for **1** and **2**, respectively). These observations suggest that upon drying volatile MeOH is exchanged into water from humid air and the replacement includes also coordinated molecules. This supposition is further supported by the elemental analysis results obtained for a freshly dried sample of **2** (reported in ESI), which show significantly higher percentage of carbon and are consistent with the composition determined from the structure (with 5 additional water molecules, which presence can be inferred from SQUEEZE). We have encountered similar EtOH to H_2O ligand exchange in the related $Ni^{II}_9W^{V}_6$ clusters containing bpy derivatives and solvent ligands on the cluster surface.[10] The removal or replacement of coordinated molecules in solid state are the basis of topotactic reactions, which often result in changes of dimensionality and magnetic properties.[19]

Despite the fact that Mo(IV) and W(IV) octacyanocyanometallates usually form isostructural compounds, in the studied reactions we observed marked differences between the two metals. The synthesis of compound **3**, which is a Mo-based analogue of **2**, required modification of synthetic conditions and resulted in poor quality crystals. The attempted synthesis of W analogue of **1**, despite efforts put into optimisation of reaction conditions, gave only colloidal non-homogenous precipitates unsuitable for further characterisation. We have also made an attempt to replace the diamagnetic octacyanometallates(IV) of group 6 with paramagnetic $[Nb(CN)_8]^{4-}$. However, due to lower stability of octacyanoniobate(IV), it resulted in fast decomposition of $[Nb(CN)_8]^{4-}$ and formation of pink crystals of an earlier characterised ionic compound $[Ni(bpy)_3][Ni(CN)_4]\cdot 6H_2O\cdot 0.5bpy$.[20]

Structure description

The structure data and refinement details for the Ni_8M_4 clusters **1** and **2** are presented in Table 1. Both compounds are composed of dodecanuclear CN-bridged clusters comprising M^{IV} complexes and Ni^{II} ions with decorating diimine: phen (**1**) or bpy (**2**) and solvent ligands. They show the same topology of the cluster core (Figure 2), which can be described as defective face-sharing cubes. The corners of the cubes are occupied by alternating Ni(II) and M(IV) ions. Because of the Ni(II)-M(IV) ratio, which is 2:1, each cube is missing one M(IV) corner and possesses an additional decorating Ni(II) cation instead. The clusters are centrosymmetric with the middle of the shared face located in an inversion centre. The asymmetric unit (Figures S2 and S3) comprises two M(IV) and four Ni(II) centres: M1 and Ni1 located at the shared-face, M2, Ni3 and Ni4 located at the outer defective face and Ni2 - the decorating ion. For regular stacked-cubes topology the outer nodes should be three-connected and the nodes of the shared face four connected. Because of the presence of the decorating Ni2, the octacyanometallates form more CN-bridges: the outer M2 ions four and M1 of the shared face five. Conversely, Ni1 located at the shared face is connected only to three M neighbours, with one diimine ligand and one H_2O completing its octahedral coordination. The other Ni ions form two CN-bridges each and their coordination sphere is completed by one diimine and two solvent molecules (water or methanol).

The cluster cores in both compounds show amazing similarity, going down to details like deformation of CN-bridges (Figure 3). To analyse the geometry of the cluster core and assess the degree of resemblance between **1** and **2** we examined the values of the corresponding angles between bridged metal centres as well as bond angles of bridging ligands (Table 2 and Table S1 in ESI).The angles between metal centres in **1** and **2** are of comparable values with the largest difference of 4.55°, which reflects close matching of the core structures. Because the angles between the CN ligands in octacyanometallates are lower than 90°, which is characteristic for hexacyanometalates, the cubes are highly distorted. The shared face has the shape of a rhombus with angles close to 80° at M1 centres and 100° at Ni1 centres. Such a large angle is achieved partly due the distortion of the octahedral coordination at Ni1 and partly by the bending of CN-bridges. The distortion is even larger at the external faces with the Ni3-M2-Ni4 angle exceeding 140°. It is caused by the presence of the additional decorating Ni2 ion, which pushes out Ni3 and partly also Ni4. For the bridging CN ligands the M-C-N angles are typically close to 180° with the largest deviation of 5.2° observed for W2-C11-N11 (Table S1 in ESI). Conversely, the Ni-N-C angles often depart from linearity. On average they are more bent in **1**, lying in the range of 153.4 - 175.4°, as compared to 156.9 - 178.9° for **2**. The most bent bridges are between Ni3 and M1 and between Ni2 and Mo1, which can be attributed to the fact that Ni2 (decorating ion) and Ni3 are bound to the same pair of octacyanometallates and repel each other.

In order to further asses the similarity of the two structures the geometry of their coordination polyhedra was analysed by means of continuous shape measure parameters (CSM),[18] which are listed in Table 3. For octacyanometallates four most commonly encountered geometries were analysed: square antiprism (SAPR-8), trigonal dodecahedron (TDD-8), biaugmented trigonal prism (BTPR-8) and Johnson biaugmented trigonal prism (JBTPR-8). The coordination geometry of the M1 centres of the shared faces for **1** and **2** is very close to that of a square antiprism, with three terminal CN-ligands divided between two square faces of the antiprism. Conversely, the coordination spheres of the peripheral M2 centres differ for **1** and **2**. The geometry of Mo2 in **1** is very close to that of a trigonal dodecahedron, while W2 in **2** shows an intermediate geometry between SAPR-8 and TDD-8, with the continuous shape measure parameters for both polyhedra of nearly the same value. Closer analysis of C-M2-C angles (Table S1) shows that the difference in coordination geometry of the outer M2 ions between **1** and **2** is caused mainly by different layout of terminal CN groups, while the bridging ligands show almost identical spatial arrangement in both compounds, which can be clearly seen in Figure 3. The terminal ligands of M2, which protrude from the surface of the clusters are affected by intermolecular interactions, most probably hydrogen bonds. However, due to severe disorder of the crystallisation solvent they could not be located.

The coordination geometry of all Ni ions in both compounds is close to octahedral (OC-6). The distortion, reflected by CSM parameters in the rage of 0.241 - 0.477, is caused mainly by the presence of rigid diimine blocking ligands, which enforce bite angle close to 80° (Table S1). Slight differences in the coordination environment of Ni is also caused by intermolecular π-π interactions between aromatic rings of diimine ligands as well as H-bonds between coordinated and uncoordinated solvent.

Despite the similarity of their cores, the clusters show different arrangement in the crystal structure (Figure 4), connected with alteration in the structure of decorating ligands. Compound **1** crystallises in space group P-1 and its unit cell comprises one cluster. Therefore all clusters have the same orientation - they are arranged in stacks along the *a* axis. In compound **2**, which crystallises in space group $P2_1/n$, there are two clusters in the unit cell in two different orientations related by a 2_1 screw axis parallel to the *b* axis. The clusters located at the corners of the unit cell form stacks along the *a* axis in a very similar way to **1**. However, they are separated by stacks of clusters located in the centre of the unit cell. Both structures are stabilised by π-π interactions (Figure 5). In **1** they form double links in [110] direction between phen ligands of Ni3-Ni4 pairs and single links along the *c* axis through the phen ligands coordinated to Ni3 cations of neighbouring clusters. In the structure of **2** only the bpy ligands coordinated to Ni3 show π-π interactions forming a chain along the *b* axis. The structure of **2** is further stabilised by a net of hydrogen bonds, which spreads in all directions (Figure S4). They connect terminal CN groups and H_2O/MeOH ligands coordinated to Ni ions through crystallisation solvent molecules. In the structure of **1** most of the crystallisation solvent is highly disordered. It was possible to locate only one partly occupied position of crystallisation water, where the molecule is trapped in a rift on the cluster surface between two coordinated solvent molecules (Figure S5).

The described dodecanuclear $Ni^{II}_8M^{IV}_4$ structures are among the largest known CN-bridged clusters, which include two large families of $M_8M'_6$ face-centred cubes (based on hexa- and terta- coordinated cynanometallates)[5] and $M_9M'_6$ six-capped body centred cubes (based on octacyanometallates)[8-10] as well as single examples of larger structures: $M_8M'_7$ vertex-sharing cubes,[21] $M_{12}M'_6$ decorated ring,[11] $M_{13}M'_7$ open winged cage[12] and $M_{15}M'_{12}$ vertex-sharing face-centred cubes.[22] **1** and **2** exhibit unique topology of face-sharing defective cubes, which was never observed before for CN-bridged assemblies. Moreover, among octacyanometallate-based clusters only two topological motives - the simplest square motif and the characteristic $M^{II}_9M^{V}_6$ body-centred six-capped cube - are represented by abundant examples. All other topologies are demonstrated either by unique structures or by small families of isostructural compounds.[2] Therefore, the dodecanuclear face-sharing defective cubes presented here are only the second example of a complex octacyanometallate-based cluster topology represented by more than one structure.

Magnetic properties

The temperature dependence of magnetic susceptibility at the applied field of 1000 Oe and magnetization *vs.* field at 1.8 K for **1** and **2** are presented in Figures 6 and 7. The χT product in the high temperature limit is about 9.0 for **1** and 9.4 cm^3Kmol^{-1} for **2** and it remains constant down to 30 K. Linear fit of 1/χ *vs*. T in the range of 1.8 to 300 K returns the Curie constants of 9.05 (**1**) and 9.42 (**2**). These values are consistent with the presence of eight isolated Ni ions with spin s = 1. The experimental g factors are 2.13 (**1**) and 2.17 (**2**), which is close to the typical value of 2.2 observed for Ni^{II} in octahedral environment. The magnetization exhibits slow increase, initially linear, with increasing field. The values at 70 kOe (12.8 and 14.1 Nβ for **1** and **2**, respectively) are much lower than the expected maximum of 17.6 Nβ, which shows that the experimental curves do not reach saturation. These results are in agreement with the expected paramagnetic behaviour of the compounds in which Ni centres are isolated by long N-C-M^{IV}-C-N diamagnetic links. The drop of χT below 30 K and small negative values of θ (-1.13 and -0.39, respectively) may be attributed to weak antiferromagnetic interactions between the Ni cations within the clusters and the effect of zero-field splitting of the Ni(II) centres in distorted octahedral environment.

In summary, we have obtained three large $Ni^{II}_8M^{IV}_4$ cluster compounds based on octacyanometallates(IV) and Ni(II) with diimine blocking ligands. They present unique topology of defective face-sharing cubes with compact cluster core surrounded by decorating ligands. Apart from the family of $M^{II}_9M^{V}_6$ body-centred six-capped cubes they are the only example of a complex octacyanometallate-based cluster topology represented by more than one structure. Due to the presence of diamagnetic M(IV) centres the compounds show paramagnetic behaviour.

Supplementary information

CCDC 1056668 (**1**) and CCDC 1056669 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We acknowledge the financial support of the Polish National Science Centre (research grant 2011/01/B/ST5/00716) and the Polish Ministry of Science and Higher Education (Diamond Grant 0195/DIA/2013/42). The research was in part carried out with the equipment purchased with the support of the European Regional Development Fund within the Polish Innovation Economy Operational Program (POIG.02.01.00-12-023/08).

References

1. M. Shatruk, C. Avendano, K. R. Dunbar, *Progress in Inorganic Chemistry*, Karlin, K. D., Ed.; John Wiley & Sons, Inc., 2009; Volume 56, 155-334;
2. D. Pinkowicz, R. Podgajny, B. Nowicka, S. Chorazy, M. Reczyński, B. Sieklucka *Inorg. Chem. Front.*, 2015, **2**, 10-27.
3. T. S. Venkatakrishnan, C. Desplanches, R. Rajamani, P. Guionneau, L. Ducasse, S. Ramasesha, J.-P. Sutter, *Inorg. Chem.* 2008, **47**, 4854–4860; J. Wang, Y.-L. Xu, H.-B. Zhou, H.-S. Wang, X.-J. Song, Y. Song, X.-Z. You, *Dalton Trans.*, 2010, **39**, 3489–3494;
4. E. J. Schelter, F. Karadas, C. Avendano, A. V. Prosvirin, W. Wernsdorfer, K. R. Dunbar, *J. Am. Chem. Soc.*, 2007**, 129**, 8139-8149; D. Li, S. Parkin, G. Wang, G. T. Yee, R. Clérac, W. Wernsdorfer, S. M. Holmes, *J. Am. Chem. Soc.*, 2006, **128**, 4214-4215; K. Mitsumoto, H. Nishikawa, G. N. Newton, H. Oshio, *Dalton Trans.*, 2012, **41**, 13601-13608; D. Li, R. Clérac, O. Roubeau, E. Harté, C Mathonière,. R. Le Bris, S. M. Holmes,, *J. Am. Chem. Soc.*, 2007, **130**, 252-258.
5. J. Y. Yang, M. P. Shores, J. J. Sokol,; J. R. Long, *Inorg. Chem.* 2003, **42**, 1403-1419; L. Jiang, H. J. Choi, X.-L. Feng, T.-B. Lu, J. R. Long, *Inorg. Chem.* 2007, **46**, 2181-2186; S. Wang, J.-L. Zuo, H.-C Zhou,. H. J. Choi, Y. Ke, J. R. Long, X.-Z. You, *Angew. Chem. Int. Ed.* 2004, **43**, 5940-5943.
6. B. Sieklucka, J. Szklarzewicz, T. J. Kemp, W. Errington, *Inorg. Chem.*, 2000, 39, 5156–5168; C. Mathoniere, R. Podgajny, P. Guionneau, C. Labrugere, B. Sieklucka, *Chem. Mater.*, 2005, **17**, 442–449; X. Chen, P. Yang, S.-L. Ma, S. Ren, M.-Y. Tang, Y. Yang. Z.-J. Guo, L.-Z. Liu, *J. Struc. Chem.*, 2009, **50**, 495–499; T. S. Venkatakrishnan, R. Rajamani, S. Ramasesha, J.–P. Sutter, *Inorg. Chem.*, 2007, **46**, 9569–9574; S.–L. Ma, Y.Ma, S. Ren, S.–P. Yan, D.–Z. Liao, *Struct. Chem.*, 2008, **19**, 329–338.
7. T. S. Venkatakrishnan, I. Imaz, J.–P. Sutter, *Inorg. Chim. Acta*, 2008, **361**, 3710-3713.
8. J. Larionova, M. Gross, M. Pilkington, H. Andres, H. Stoeckli-Evans, H. U. Güdel, S. Decurtins, *Angew. Chem. Int. Ed.*, 2000, **39**, 1605-1609; S.-L. Ma, S. Ren, Y. Ma, D.-

Z. Liao, S.-P. Yan, *Struct. Chem.*, 2009, **20**, 161-167; Z. J. Zhong, H. Seino, Y. Mizobe, M. Hidai, A. Fujishima, S. Ohkoshi, K. Hashimoto, *J. Am. Chem. Soc.*, 2000, **122**, 2952-2953; D. E. Freedman, M. V. Bennett, J. R. Long, *Dalton Trans.*, 2006 2829-2834. Y. Song, P. Zhang, X.-M. Ren, X.-F. Shen, Y.-Z. Li, X.-Z. You, *J. Am. Chem. Soc.*, 2005, **127**, 3708-3709; F. Bonadio, M. Gross, H. Stoeckli-Evans, S. Decurtins, *Inorg. Chem.*, 2002, **41**, 5891-5896.

9. J.H. Lim, H.S. Yoo, J.I. Kim, J.H. Yoon, N. Yang, E.K. Koh, J.–G. Park, C.S. Hong, *Eur. J. Inorg. Chem.*, 2008, 3428–3431; J. H. Lim, H. S. Yoo, Y. H. Yoon, E. K. Koh, H. C. Kim, C. S. Hong, *Polyhedron*, 2008, **27**, 299–303. M. G. Hilfiger, H. Zhao, A. Prosvirin, W. Wernsdorfer and K. R. Dunbar, *Dalton Trans.* 2009, 5155–5163;
10. B. Nowicka, K. Stadnicka, W. Nitek, M. Rams, B. Sieklucka, *CrystEngComm* 2012, **14**, 6559 - 6564.
11. R. Pradhan, C. Desplanches, P. Guionneau, J.–P. Sutter, *Inorg. Chem.*, 2003, **42**, 6607–6609; D.-P. Zhang, L.-F. Zhang, G.-L. Li, Z.-H. Ni, *Chem. Commun.*, 2013, **49**, 9582-9584.
12. J. Wang, Z.-C. Zhang, H.-S. Wang, L.-C. Kang, H.-B. Zhou, Y. Song, X.-Z. You, *Inorg. Chem.*, 2010, **49**, 3101-3103.
13. J. G. Leipoldt, L. C. D. Bok, P. J. Cilliers, Z. Anorg. Allg. Chem., 1974, **409**, 343. J. G. Leipoldt, L. C. D. Bok and P. J. Cilliers, *Z. Anorg. Allg. Chem.*, 1974, **407**, 350.
14. G. M. Sheldrick, *Acta Crystallogr. A.*, 2008, **64**, 112-122.
15. SHELXL-2013, Program for the refinement of crystal structures, G. M. Sheldrick, University of Göttingen, 2013.
16. A. L. Spek, *Acta Cryst. D*, 2009, **65**, 148-155.
17. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453–457.
18. M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez: *SHAPE v. 2.1*, University of Barcelona, Barcelona, Spain, 2013.
19. D. Pinkowicz, R. Podgajny, B. Gaweł, W. Nitek, W. Łasocha, M. Oszajca, M. Czapla, M. Makarewicz, M. Bałanda, B. Sieklucka *Angew. Chem. Int. Ed.* 2011, **50**, 3973–3977; W. Kaneko, M. Ohba, S. Kitagawa, *J. Am. Chem. Soc.* 2007, **129**, 13706–13712; D. Pinkowicz, R. Podgajny, M. Bałanda, M. Makarewicz, B. Gaweł, W. Łasocha, B. Sieklucka, Inorg. Chem.2008, 47, 9745 – 9747.
20. J. Černak, E. Lengyelova, K. Ahmadi, A.-M. Hardy, *J. Coord. Chem.* 1996, **37**, 55-62.
21. S. M. Contakes, M. L. Kuhlman, M. Ramesh, S. R. Wilson, T. B. Rauchfuss, *Proc. Nat. Ac. Sci. USA*, 2002, **99**, 4889-4893.
22. J. J. Sokol, M. P. Shores, J. R. Long, *Inorg. Chem.* 2002, **41**, 3052-3054.

Table 1 Crystallographic data for compounds **1** and **2**

	(**1**)	(**2**)
Empirical formula	$C_{130.60}H_{98.40}Mo_4N_{48}Ni_8O_{14.60}$	$C_{116}H_{130}N_{48}Ni_8O_{29}W_4$
Formula weight	3427.21	3865.76
Temperature / K	200(2) K	150(2) K
Crystal system	triclinic	monoclinic
Space group	P–1	$P2_1/n$
a /Å	14.1796(5)	13.6083(3)
b /Å	15.6667(7)	20.4045(3)
c /Å	21.9922(9)	28.7109(5)
α / °	95.044(3)	90
β / °	107.310(3)	102.4260(10)
γ / °	109.261(3)	90
Volume / $Å^3$	4308.3(3)	7785.4(2)
Z	1	2
Density (calc.) / Mg/m^3	1.321	1.649
Absorption coeff. / mm^{-1}	1.196	3.963
F(000)	1727	3828
Crystal size / mm	0.06 x 0.08 x 0.17	0.11 x 0.10 x 0.09
Theta range / °	1.41 to 25.00	1.23 to 25.00
Reflections collected	32078	48958
R_{int}	0.0667	0.0516
Independent reflections	15040	13708
Reflections with $I<4\sigma(I)$	11128	10336
Parameters	947	953
GOF on F^2	1.020	1.045
R indices [$I>2\sigma(I)$]	R1 = 0.0591	R1 = 0.0499
	wR2 = 0.1542	wR2 = 0.1059
R indices (all data)	R1 = 0.0767	R1 = 0.0748
	wR2 = 0.1630	wR2 = 0.1150

Table 2 Angles (°) between CN-bridged metal centres in **1** and **2**

angle	**1**	**2**	angle	**1**	**2**
Ni1-M1-Ni1'	77.99	81.71	Ni1-M2-Ni3	75.99	77.21
Ni1-M1-Ni2	77.00	77.34	Ni1-M2-Ni4	73.01	73.16
Ni1'-M1-Ni2	66.86	66.98	Ni2-M2-Ni3	66.54	66.32
Ni1-M1-Ni3	76.82	78.29	Ni2-M2-Ni4	87.58	83.03
Ni1'-M1-Ni3	131.32	132.87	Ni3-M2-Ni4	143.41	141.27
Ni1-M1-Ni4'	111.36	111.23	M1-Ni1-M1'	102.01	98.29
Ni1'-M1-Ni4'	72.53	72.89	M1-Ni1-M2	91.56	91.22
Ni2-M1-Ni3	67.30	67.17	M1'-Ni1-M2	102.31	102.31
Ni2-M1-Ni4'	135.68	137.27	M1-Ni2-M2	92.95	92.18
Ni3-M1-Ni4'	156.04	156.75	M1-Ni3-M2	92.90	91.69
Ni1-M2-Ni2	76.62	77.13	M1'-Ni4-M2	102.94	103.03

Table 3 Continuous shape measure parameters for coordination spheres of Mo, W and Ni calculated with SHAPE 2.1;[18] SAPR-8 = square antiprism, TDD-8 = trigonal dodecahedron, BTPR-8 = biaugmented trigonal prism, JBTPR-8 = Johnson biaugmented trigonal prism, OC-6 = octahedron

Deviation from ideal geometry of common coordination polyhedra for $[M(CN)_8]^{4-}$				
	SAPR-8	TDD-8	BTPR-8	JBTPR-8
Mo1	0.432	1.375	1.787	2.351
W1	0.264	2.002	1.652	2.264
Mo2	1.588	0.553	1.456	2.054
W2	0.934	0.937	1.667	2.259
Deviation from ideal octahedral geometry (OC-6) for Ni^{2+} ions				
	Ni1	Ni2	Ni3	Ni4
1	0.278	0.273	0.477	0.241
2	0.333	0.297	0.327	0.337

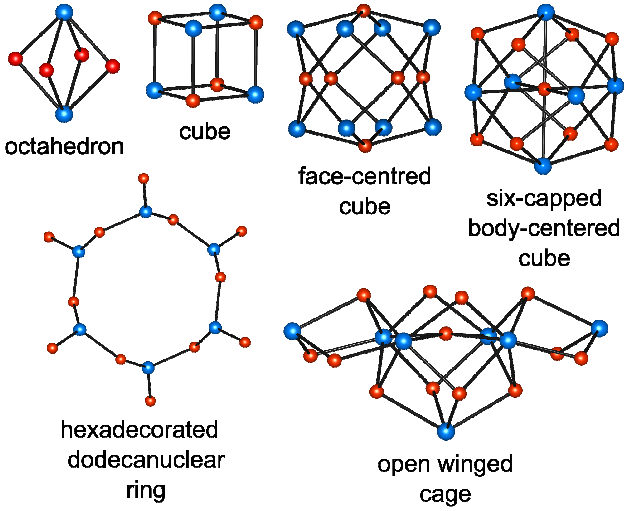


Figure 1. Topologies of large CN-bridged clusters.

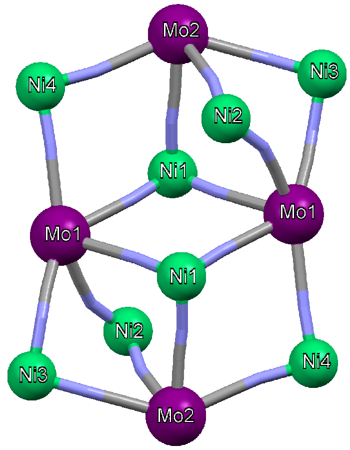


Figure 2. Cluster core of **1**, only metal centres and bridging ligands shown; N - blue sticks, C - grey sticks.

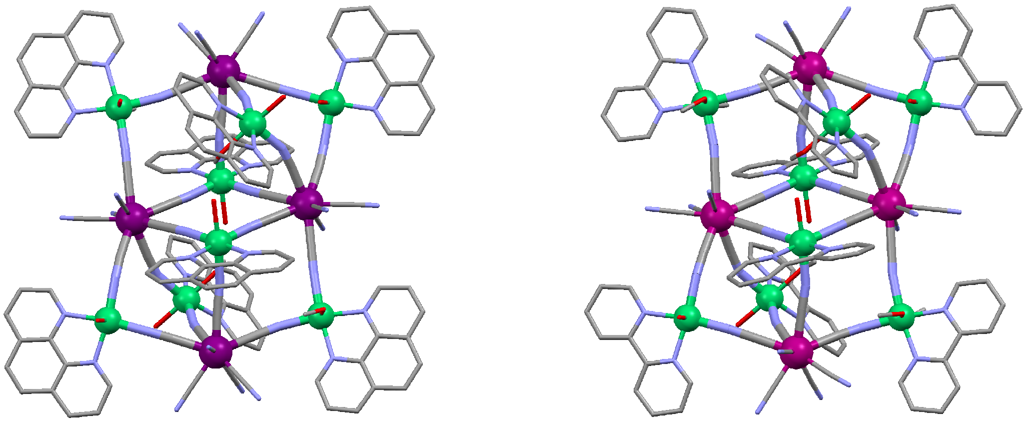


Figure 3. Cluster structures of **1** (left) and **2** (right); Ni - green balls, Mo and W - purple balls, N - blue sticks, C - grey sticks, O - red sticks; hydrogen atom omitted for clarity.

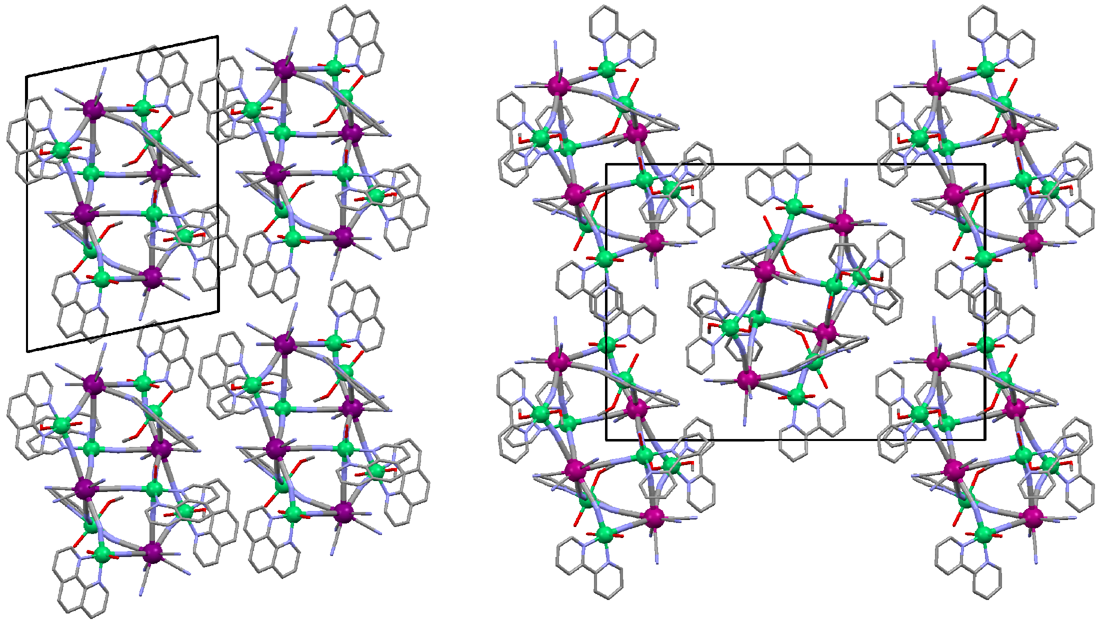


Figure 4. Packing diagrams of **1** (left) and **2** (right); view along *a* axis.

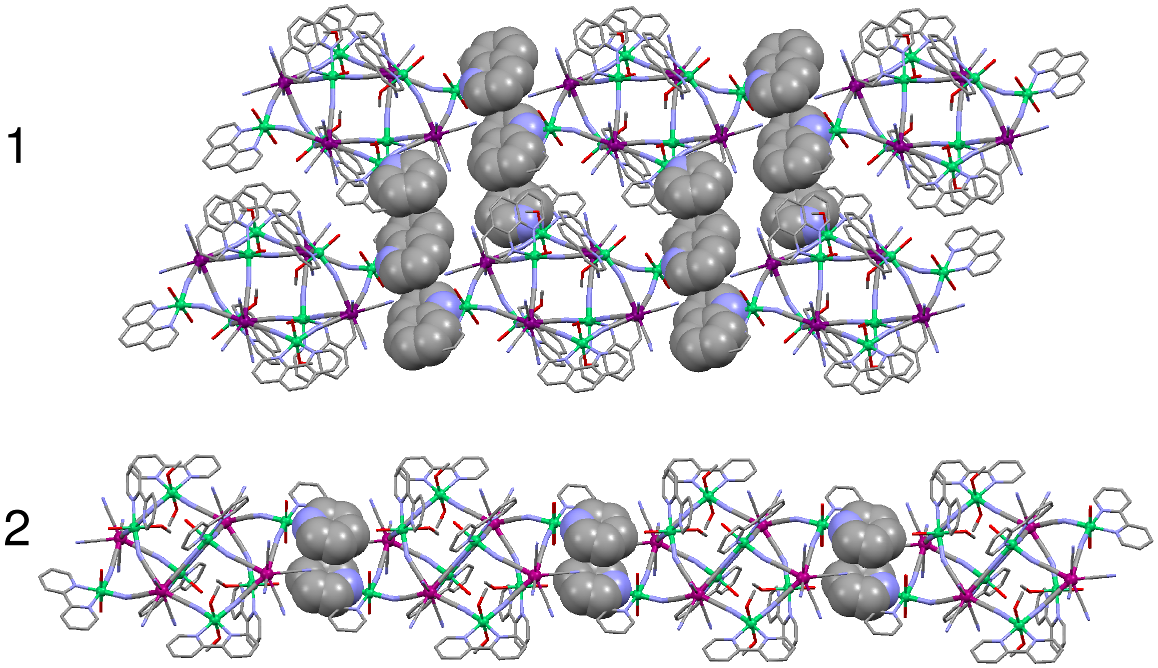


Figure 5. π-π interactions linking clusters in two directions in **1** and one direction in **2**.

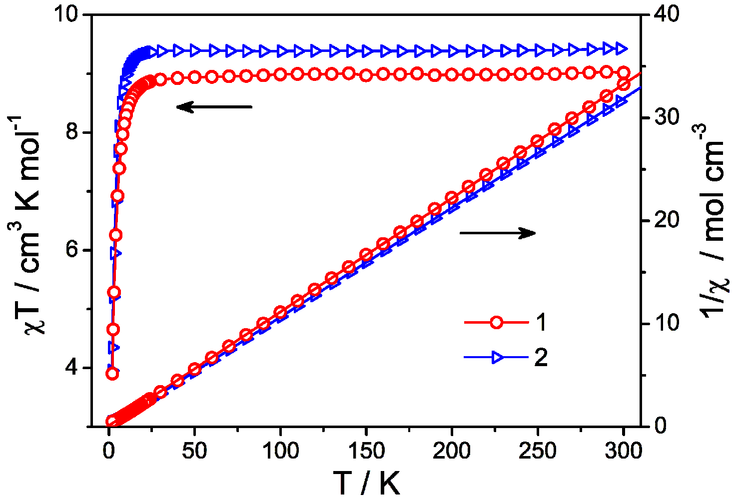


Figure 6. Temperature dependence of magnetic susceptibility at the applied field of 1 kOe for **1** and **2**.

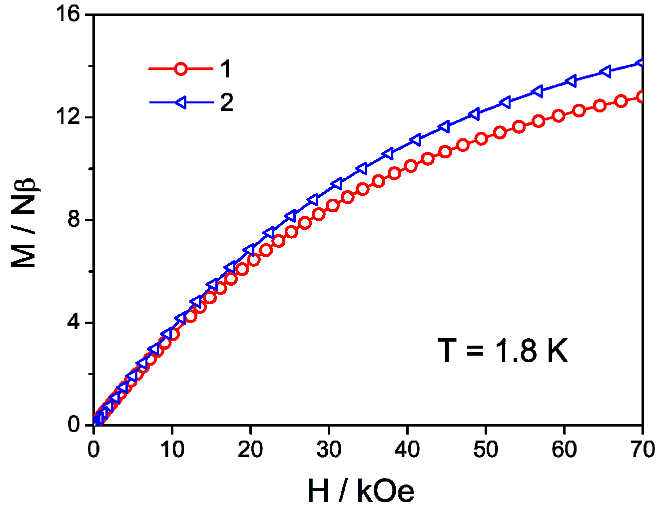


Figure 7. Magnetisation *vs.* field at 1.8 K for **1** and **2**.

Graphical abstract

The same frame in different decorations: two structures with the same unique topology of CN-bridged core - rarity among octacyanometallate-based clusters.