Accepted Manuscript

Hetero-octanuclear cubane-like and one-dimensional cyano complexes with the N,N-dimethylendiamine ligand

Güneş Süheyla Kürkç üoğlu, Okan Zafer Yeşilel, Mehran Aksel, Orhan Büyükgüngör

PII:	S0277-5387(14)00625-1
DOI:	http://dx.doi.org/10.1016/j.poly.2014.09.019
Reference:	POLY 10987
To appear in:	Polyhedron
Received Date:	20 June 2014
Accepted Date:	8 September 2014



Please cite this article as: G.S. Kürkç üoğlu, O.Z. Yeşilel, M. Aksel, O. Büyükgüngör, Hetero-octanuclear cubanelike and one-dimensional cyano complexes with the N,N-dimethylethylenediamine ligand, *Polyhedron* (2014), doi: http://dx.doi.org/10.1016/j.poly.2014.09.019

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Hetero-octanuclear cubane-like and one-dimensional cyano complexes with

the N,N-dimethylethylenediamine ligand

Güneş Süheyla Kürkçüoğlu,^{*a} Okan Zafer Yeşilel,^b Mehran Aksel,^c and Orhan Büyükgüngör^d

^aEskişehir Osmangazi University, Faculty of Arts and Sciences, Department of Physics, 26480 Eskişehir, Turkey

^bEskişehir Osmangazi University, Faculty of Arts and Sciences, Department of Chemistry, 26480 Eskişehir, Turkey

^cAdnan Menderes University, Faculty of Medicine, Department of Biophysics, 09100, Aydın, Turkey

^dOndokuz Mayıs University, Faculty of Arts and Sciences, Department of Physics 55139 Samsun, Turkey

Abstract

A series of complexes containing dmen (dmen = N,N-dimethylethylenediamine) units and cyano groups, namely bimetallic octanuclear and binuclear $[Zn_4(dmen)_8Ni_4(CN)_{16}]$ (1), $[Cd_4(dmen)_8Ni_4(CN)_{16}]$ (2), $[Zn(dmen)_2Pd(\mu-CN)_2(CN)_2]$ (3) and $[Cd(dmen)_2Pd(\mu-CN)_2(CN)_2]$ (4), have been synthesized and characterized by elemental, spectral (FT-IR and Raman) and thermal analyses techniques. The molecular structures of the complexes have been determined by the single crystal X-ray diffraction technique. The X-ray analyses of 1 and 2 show heterometallic octanuclear cubane-like structures in which Zn(II) or Cd(II) and Ni(II) ions reside in alternate corners, whereas complexes 3 and 4 display one-dimensional chain structures.

Keywords: Hetero-octanuclear complexes; Cubane-like complexes; N,Ndimethylethylenediamine complexes; Tetracyanonickelate complexes; Tetracyanopalladate complexes.

*Corresponding author. Tel.: +90 222 2393750; Fax: +90 222 2393578.

E mail: gkurkcuo@ogu.edu.tr (G.S. Kürkçüoğlu)

1. Introduction

Homo- and heterometallic cubane-like cluster complexes are known for a wide variety of transition metals and they appear to be one of the most important common basic structures of transition metal cluster complexes [1,2]. Homometallic Mo_4S_4 cubane-type clusters have been known for some 20 years [3,4]. The $[M(CN)_8]^{3-,4-}$ (M = Mo, W, Nb) units exhibit various geometrical structures such as square antiprism, dodecahedron and bicapped trigonal prism, and the cyanide group is a good bridging building block for transition metal complexes. These characteristics enable them to be potential building blocks to construct various architectures.

The ability of the cyano group to link various central atoms has been used in organometallic and coordination chemistry for the construction of various super complexes or molecular assemblies [5-7] and in the field of supramolecular chemistry for building various 1D, 2D or 3D structures [8-13]. Cyano complexes with polymeric structures can mimic naturally occurring minerals [14-16] and form various types of host-guest systems [17-19]. It is known that hexacyanometallates react with simple metal ions to produce Prussian blue and its analogues [8,20-23] and with metal complexes to generate mixed valence multidimensional networks [24-27]. The crystal structures of a number of cyano-bridged complexes involving transition metal ions have been reported [12,28], including some trimeric [29] and polymeric species [30].

The dimensionality of the formed structure can be tuned by bonding to several coordination sites on the central atom of the complex cation. Using this approach a large number of inorganic-organic hybrid materials based on cyano complexes were synthesized and structurally and magnetically characterized [31-34]. Zn(II) and Cd(II) ions, as the cationic

central atom in cyano complexes, generally adopt a coordination number of six. We are interested in the synthesis, spectral and structural characterization of cyano complexes [35-38]. In preceding studies, some complexes of N,N-dimethylethylenediamine with metal(II) ions were described in several papers [39-45]; however, to the best our knowledge, neither crystallographic nor spectroscopic data have been reported so far that would explicitly allow the structural analyses of octanuclear cubane-like structures with Zn(II) and Cd(II) N,N-dimethylethylenediamine complexes of tetracyanonickelate(II) or tetracyanopalladate(II) ions.

Previously, we have characterized several cyano complexes, [Cd(deten)₂Ni(µ- $CN_{2}(CN)_{2}_{n}$ [46], [Zn(deten)_{2}Pd(\mu-CN)_{2}(CN)_{2}_{n} and [Cd(deten)_{2}Pd(\mu-CN)_{2}(CN)_{2}_{n} [47]] (deten = N,N-diethylethylenediamine). As a part of our continuing research on the syntheses and characterizations of complexes, we define in this study, the syntheses, spectral (FT-IR and Raman), thermal and elemental analyses $[Zn_4(dmen)_8Ni_4(CN)_{16}]$ (1), of $[Cd_4(dmen)_8Ni_4(CN)_{16}]$ (2), $[Zn(dmen)_2Pd(\mu-CN)_2(CN)_2]$ (3) and $[Cd(dmen)_2Pd(\mu-CN)_2(CN)_2]$ CN)2(CN)2] (4). The molecular and crystal structures of the cyano-bridged heteronuclear complexes 1–4 have been determined by X-ray single crystal diffraction. The thermal decomposition behaviors of the complexes were followed up in the temperature range 30-700 °C in a static air atmosphere.

2. Experimental

2.1. Materials and measurements

All chemicals used were analytical reagents and commercially purchased. FT-IR and Raman spectra were obtained with a Perkin Elmer spectrum100 FT-IR spectrometer using KBr pellets in the 4000-400 cm⁻¹ range and a Brucker Senterra Dispersive Raman spectrometer in the 4000-250 cm⁻¹ range, respectively. Elemental analyses for C, H and N were performed using a Leco CHNS-932 Analyser. A Perkin Elmer Diamond TG/DTA

Thermal Analyzer was used to record simultaneous TG, DTG and DTA curves in a static air atmosphere at a heating rate of 10 °C min⁻¹ over the temperature range 30-700 °C using platinum crucibles.

2.2. Preparation of the complexes

 $K_2[M'(CN)_4] \cdot H_2O$ was prepared by mixing stoichiometric amounts of the metal(II) chloride $(1 \text{ mmol}, \text{NiCl}_2 \cdot 6\text{H}_2\text{O} = 0.237 \text{ g or } \text{PdCl}_2 = 0.177 \text{ g})$ in water (10 mL) with KCN (4 mmol, 0.260 g) also in water (10 mL). These solutions were filtered and allowed to evaporate at room temperature in order to crystallize. The K₂[M'(CN)₄]·H₂O (1 mmol) complexes (M', 0.259 g for Ni(II), 0.306 g for Pd(II)) were dissolved in water (50 mL). To these solutions, 1 mmol of zinc(II) chloride or 1 mmol of cadmium(II) chloride hemi(pentahydrate) dissolved in water (10 mL) was added with continuous stirring, approximately for 4 h at 50 °C in a temperature-controlled bath. The $Zn[Ni(CN)_4] \cdot H_2O$ and $Zn[Pd(CN)_4] \cdot H_2O$ compounds obtained were filtered and dried in air. The complexes were prepared from a 50 mL of water solution of 1 mmol of Zn[Ni(CN)₄]·H₂O (0.246 g) or Zn[Pd(CN)₄]·H₂O (0.293 g), separately. To these solutions, N,N-dimethylethylenediamine (dmen) (0.352 g, 4 mmol) dissolved in ethanol (10 mL) was added with continuous stirring and after a few minutes, a few drops ammonia (5 mL, 28%) were added to the resulting solution, followed by continuous stirring approximately for 5 h at 60 °C in a temperature-controlled bath. The solutions were then filtered, and the clear solutions thus obtained were kept for crystallization at room temperature. Within about a week crystals formed. The procedure for the syntheses of the cadmium complexes was similar to that used for the zinc complexes, except that $Zn[M'(CN)_4] \cdot H_2O$ was used instead of $Cd[M'(CN)_4] \cdot H_2O$ ($Cd[Ni(CN)_4] \cdot H_2O = 0.246$ g or $Cd[Pd(CN)_4] \cdot H_2O = 0.340$ g). The freshly prepared compounds were analyzed for C, H and N and the results are illustrated Table S1.

2.3. Crystallographic analyses

Diffraction experiments were carried out at 293 K for 1 and 2, and 296 K for 3 and 4 on a Stoe IPDS diffractometer. The structures were solved by direct methods and refined using the programs SHELXL-2013 and SHELXL97 [48]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods [48]. The hydrogen atoms were placed in geometrically idealized positions and refined as riding atoms. The following procedures were implemented in our analysis: data collection, X-Area; cell refinement, X-Area; data reduction, X-RED [49]; program(s) used for molecular graphics, MERCURY [50]; software used to prepare material for publication, WinGX [51]. The crystal data and refinement details of the complexes are summarised in Table 1, and selected bond lengths and angles are collected together in Table 2. nP

3. Results and Discussion

3.1. Crystal structures of the complexes

The crystal structures of 1 and 2 with the atom labelling is shown in Fig. 1. The asymmetric unit of 1 and 2 consists of one Zn(II) or Cd(II) ion, one Ni(II) ion, two dmen ligands and four cyano ligands. Complexes 1 and 2 exhibit heterometallic octanuclear cubanelike structures. To the best of our knowledge, no complex containing an octanuclear cubanelike structure with the cyano ligand has been reported to date. Both complexes 1 and 2 are structurally similar. Single-crystal X-ray diffraction analyses revealed that the two isostructural complexes crystallize in the tetragonal crystal system, space group I41/a. Both 1 and 2 contain a cubane-like $[M_4(dmen)_8Ni_4(CN)_{16}]$ unit (M = Zn(II) or Cd(II)), which is completed by four Ni(II) and four Zn(II) or Cd(II) ions, eight dmen and sixteen cyano ligands. As shown in Figure 1, every cubane core is constructed from four Ni(II) atoms and four Zn(II) or Cd(II) ions. In 1 or 2, the Ni(II) ions are coordinated to four C atoms from cyano ligands, forming a square planar geometry, while each Zn(II) or Cd(II) atom has a slightly distorted octahedral configuration, coordinated by two N atoms from bridging cyano anions and four N

atoms from two bidentate dmen ligands. These Ni(II) and Zn(II) or Cd(II) units are linked by cyano ligands.

At the same time, intramolecular C–H…Ni short contacts between a Ni(II) center and a hydrogen atom of a methyl group of a dmen ligand are observed in complexes **1** and **2**. The H…Ni distance is 2.926(1) Å and this value is somewhat longer than the sum of the Van der Waals radii of the nickel and hydrogen atoms, which is 2.83 Å. This value is found to be similar to those of previously reported Ni(II) complexes [52-54]. The shortest Ni…Ni, Ni…Zn and Zn…Zn distances are 7.546(2), 5.076(2) and 7.826(1) Å, respectively. The crystal structures of **1** and **2** exhibit significant hydrogen bonds between the cubane-like units. Figures 2 and 3 clearly show that the cubane-like units are connected to each other by N–H…N hydrogen bonds forming three-dimensional supramolecular networks.

To further investigate the effect of the metal center, a tetracyanopalladate(II) complex was utilized in the reaction for the synthesis of complexes **3** and **4**. When the Ni(II) ion was replaced by the Pd(II) ion, we obtained complexes **3** and **4** as heterometallic one dimensional polynuclear structures. Single crystal X-ray analysis showed that **3** and **4** are isomorphous and the crystal structures indicate they are one dimensional chain polymers. Complex **3** crystallizes in the orthorhombic system, space group Pbca, whereas complex **4** crystallizes in the monoclinic system, space group P21/c. As shown in Fig. 4, the asymmetric unit of **4** consists of half Cd(II) and half Pd(II) ions, one bidentate dmen and two cyano ligands. The Cd(II) ion adopts a distorted octahedral geometry and is coordinated by six N atoms from two bidentate dmen and two cyano ligands. Four N atoms of the dmen ligand comprise the equatorial plane, while two N atoms of cyano ligands occupy the axial positions. The Pd(II) ion has a square planar coordination formed by four C atoms from cyano ligands. The Cd1…Pd1 and Cd1…Cd1ⁱ distances in the 1D chain are 5.2560(5) and 10.5120(9) Å, while

between chains the Cd1···Cd1ⁱⁱ and Cd1···Cd1ⁱⁱⁱ distances are 6.8223(6) and 9.159(1) Å, respectively [(i): x, y, -1+z, (ii) 1+x, y, z; (iii) 1+x, y, 1+z] (Fig. 5).

As a result of using tetracyanonickelate(II) or tetracyanopalladate(II) complexes, different structural complexes have been obtained. When Zn(II) and Cd(II) ions are used, the complexes obtained with tetracyanonickelate(II) exhibit a cubic structure, whilst the complexes obtained with tetracyanopalladate(II) have a 1D polynuclear structure. The reason for this difference is thought to arise from the strong C-H…Ni interactions between the methyl groups and the Ni(II) metal with a small radius.

3.2. Vibrational (FT-IR and Raman) spectra of the complexes

The FT-IR and Raman spectra of the complexes recorded in the 4000-400 and 4000-250 cm⁻¹ ranges are shown in Figs. S1 and S2, respectively. It is noted that the FT-IR data on dmen and its complexes are not plentiful in the literature. The observed frequencies in the FT-IR spectra of dmen and its complexes, their approximate intensities and probable assignments are given in Table S2. Dmen has one primary amine nitrogen atom and one tertiary amine nitrogen atom. The molecule also has CH₂ and CH₃ groups. Most liquid aliphatic primary amines absorb at 3400-3380 and 3330-3250 cm⁻¹, with a shoulder near 3200 cm⁻¹. As seen from Table S2, we assigned three bands to NH stretching vibrations of the NH₂ group in this region. If two methyl groups are attached to a nitrogen atom, two bands are found in the region 2818-2770 cm⁻¹, and it has been shown that coordination of the nitrogen atom to a metal may cause the disappearance of this band. The NH₂ group has its scissors deformation frequency at 1660-1590 cm⁻¹. We observed this mode at 1596 cm⁻¹ in dmen. The CH₂ group gives rise to a band near 1458 cm⁻¹ due to the scissoring vibrations and the asymmetric CH₃ deformation is also found around 1466 cm⁻¹. By comparison with related molecules, a strong band at 1458 cm⁻¹ in dmen is assigned to CH₂ scissoring. The C–N stretching vibration occurs in the range 1220-1020 cm⁻¹. We observed several bands in this region and assigned them

tentatively to C–N stretching vibrations of the primary and tertiary amine groups. We observed several bands in the region 1000-400 cm⁻¹ for dmen; these bands are assigned on a basis of a comparison with its complexes and related molecules.

The dmen vibrational modes observed in the FT-IR and Raman spectra of the complexes show the characteristics of a coordinated ligand. On coordination, the N–H and C– N stretching frequencies should decrease, while the C–H stretching frequency should increase, owing to the consecutive inductive effects [55]. In our case, however, this expectation is not realized for the N–H stretching modes of the NH₂ group. Such cases were observed for propylenediamine [44] and trimethylenediamine [56] complexes.

The vibrational modes of dmen observed in the FT-IR and Raman spectra of the complexes are found to be similar in frequency. We have assigned the fundamental modes of dmen on the basis of the frequency shifts of the coordinated ligand, of the group vibrational concept, infrared intensity and a comparison with the assignments for ethylenediamine [57]. The FT-IR and Raman spectra for complexes **1-4** show all the characteristic ligand frequencies: $v_{as}(NH_2)$, $v_s(NH_2)$, v(N-H), v(C-H), $\delta(NH_2)$, v(C-N) and v(C-C) in the ranges 3365-3300, 3250-3150, 3180-3150, 2980-2950, 1600-1590, 1060-1030 and 980-950 cm⁻¹, respectively. The positions of important and well identifiable bands are displayed in the experimental part and their assignment was made according to the literature [58].

The v(CN) vibrations are the most characteristic bands in cyano groups because they give a sharp and strong band and are determined easily in the 2200-2000 cm⁻¹ range. The assigned wave numbers for the v(CN) vibrations in the complexes are given in Table S3, together with the vibrational wavenumbers of $K_2Ni(CN)_4$ ·H₂O [59] and $K_2Pd(CN)_4$ ·H₂O [60]. The most characteristic features of the FT-IR spectra of all the complexes are the strong and sharp absorption bands observed at 2157 and 2130 cm⁻¹ (1), 2150 and 2130 cm⁻¹ (2), 2141 and 2130 cm⁻¹ (3), 2137 and 2130 cm⁻¹ (4). These absorption bands, in accord with the literature

[61], are attributed to v(CN) stretching vibrations of the cyano ligands. For the v(C=N) modes of $[Ni_4(CN)_{16}]$, two bands appear at 2157 and 2130 cm⁻¹ for the inter-metallic C=N and the terminal C=N stretching vibrations respectively. The observed absorption bands in complexes **1** and **2** are weakly split, indicating the non-equivalency of the cyano ligands.

The coordination of the cyano ligands to the central M(II) (Ni or Pd) atom in complexes 1-4 and thus the formation of M–C coordination bonds is suggested by the observed absorption bands at 417, 414, 417 and 415 cm⁻¹, respectively, which are attributed to the δ (M–CN) vibration. The same vibration occurs in the FT-IR spectra of the [Ni(CN)₄]²⁻ anion at 416 cm⁻¹ [61]. Absorption bands due to analogous δ (Pd–CN) and δ (Pt–CN) vibrations are usually observed at 383 and 300 cm⁻¹, respectively [40,41] (out of range for our instrument).

3.3. Thermal analyses

The thermal behaviors of **1** and **2** are quite similar and they show a two stage mass loss (Figs. S3-S4). The first stage between 115 and 333 °C for **1**, 99 and 259 °C for **2** corresponds to the exothermic (for **1**) and endothermic (for **2**) elimination of eight and four dmen ligands with a mass loss of 41.01 and 18.00 % respectively (calcd. 43.59 and 19.52 %, respectively). In the second stage, a strong exothermic peak on the DTA curve (DTAmax = 375 °C, found 22.92 %, calcd. 25.73 % for **1** and 340 °C, found 39.78 %, calcd. 42.57 % for **2**) is associated with burning of the cyano ligands for **1** and decomposition of four dmen ligands and burning of the cyano groups for **2**. The final decomposition products are identified as MO + NiO (M = Zn and Cd) [found (calculated) % = 35.66 (38.59) for **1** and 42.05 (44.98) for **2**].

The thermal behaviors of **3** and **4** are quite similar and they show a three stage mass loss (Figs. S5-S6). The first stage between 112 and 230 °C for **3**, 158 and 233 °C for **4** corresponds to the endothermic elimination one dmen ligand with a mass loss of 21.40 and 20.21%, respectively (calcd. 19.49 and 19.57, respectively). The removal of another one dmen

ligand occurs in the second stage between 230 and 328 °C for **3**, 233 and 392 °C for **4** with a mass loss of 19.11 and 19.14%, respectively (calcd. 19.49 and 19.57%, respectively). In the last stage, a strong exothermic peak on the DTA curve (DTA_{max} = 406 and 437 °C, respectively) is associated with the decomposition and burning of the cyano ligands. The thermal decomposition product was identified as ZnO+Pd or CdO+Pd.

The final decomposition product was identified by FT-IR spectroscopy by a comparison with the corresponding spectrum obtained under the same circumstances for the pure oxide.

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC NO 833233 for 1, 833235 for 2, 981139 for 3 and 863116 for 4. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-36033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

References

- [1] R. Hernandez-Molina, V.P. Fedin, M.N. Sokolov, D.M. Saysell, A.G. Sykes, Inorg. Chem.37 (1998) 4328.
- [2] Y. Cui, L. Xu, J.S. Huang, Inorg. Chim. Acta 277 (1998) 130.
- [3] T. Shibahara, Adv. Inorg. Chem. 37 (1991) 143.
- [4] S. Harris, Polyhedron 8 (1989) 2843.

[5] M. Fritz, D. Rieger, E. Bar, G. Beck, J. Fuchs, G. Holzmann, W.P. Fehlhammer, Inorg. Chim. Acta 198 (1992) 513.

- [6] P. Braunstein, B. Oswald, A. Decian, J. Fischer, J. Chem. Soc., Dalton Trans. (1991) 2685.
- [7] M.J. Scott, R.H. Holm, J. Am. Chem. Soc. 116 (1994) 11357.
- [8] T. Mallah, S. Thiebaut, M. Verdaguer, P. Veillet, Science 262 (1993) 1554.
- [9] T. Soma, H. Yuge, T. Iwamoto, Angew. Chem. Int. Ed. Engl. 33 (1994) 1665.
- [10] H. Henkel, D. Babel, Z. Naturfors. B 39 (1984) 880.
- [11] D.W. Knoeppel, S.G. Shore, Inorg. Chem. 35 (1996) 1747.
- [12] M. Ohba, H. Okawa, T. Ito, A. Ohto, J. Chem. Soc., Chem. Comm. (1995) 1545.
- [13] H.X. Zhang, Y.X. Tong, Z.N. Chen, K.B. Yu, B.S. Kang, J. Organomet. Chem. 598(2000) 63.
- [14] T. Iwamoto, S. Nishikiori, T. Kitazawa, Supramol. Chem. 6 (1995) 179.
- [15] T. Iwamoto, in: Chemical Physics of Intercalation II, Plenum Press, New York, 1993, pp. 325.
- [16] T. Kitazawa, J. Incl. Phenom. Mol. 26 (1996) 153.
- [17] T. Iwamoto, J Incl. Phenom. Mol. 24 (1996) 61.
- [18] T. Soma, T. Iwamoto, Mol. Cryst. Liq. Crys. A 276 (1996) 19.
- [19] B.F. Abrahams, B.F. Hoskins, R. Robson, J. Chem. Soc., Chem. Comm. (1990) 60.
- [20] V. Gadet, T. Mallah, I. Castro, M. Verdaguer, P. Veillet, J. Am. Chem. Soc. 114 (1992)9213.
- [21] F. Herren, P. Fischer, A. Ludi, W. Halg, Inorg. Chem. 19 (1980) 956.
- [22] W.R. Entley, G.S. Girolami, Science 268 (1995) 397.
- [23] M. Verdaguer, Science 272 (1996) 698.
- [24] H.Z. Kou, S. Gao, W.M. Bu, D.Z. Liao, B.Q. Ma, Z.H. Jiang, S.P. Yan, Y.G. Fan, G.L.
- Wang, J. Chem. Soc., Dalton Trans. (1999) 2477.
- [25] M. Ohba, N. Usuki, N. Fukita, H. Okawa, Inorg. Chem. 37 (1998) 3349.

- [26] H.Z. Kou, W.M. Bu, D.Z. Liao, Z.H. Jiang, S.P. Yan, Y.G. Fan, G.L. Wang, J. Chem. Soc., Dalton Trans. (1998) 4161.
- [27] M. Ferbinteanu, S. Tanase, M. Andruh, Y. Journaux, F. Cimpoesu, I. Strenger, E. Riviere, Polyhedron 18 (1999) 3019.
- [28] M. Ohba, H. Okawa, N. Fukita, Y. Hashimoto, J. Am. Chem. Soc. 119 (1997) 1011
- [29] N. Mondal, S. Mitra, G. Rosair, Polyhedron 20 (2001) 2473.
- [30] N. Mondal, M.K. Saha, B. Bag, S. Mitra, V. Gramlich, J. Ribas, M.S. El Fallah, J. Chem. Soc., Dalton Trans. (2000) 1601.
- [31] M. Ohba, H. Okawa, Coord. Chem. Rev. 198 (2000) 313.
- [32] X.P. Shen, S. Gao, G. Yin, K.B. Yu, Z. Xu, New J. Chem. 28 (2004) 996.
- [33] J. Larionova, S. Willemin, B. Donnadieu, B. Henner, C. Guerin, B. Gillon, A. Goujon, J Phys. Chem. Solids 65 (2004) 677.
- [34] X.Y. Chen, W. Shi, J. Xia, P. Cheng, B. Zhao, H.B. Song, H.G. Wang, S.P. Yan, D.Z.
- Liao, Z.H. Jiang, Inorg. Chem. 44 (2005) 4263.
- [35] G.S. Kürkçüoğlu, T. Hökelek, O.Z. Yeşilel, S. Aksay, Struct. Chem. 19 (2008) 493.
- [36] G.S. Kürkçüoğlu, O.Z. Yeşilel, I. Kavlak, O. Büyükgüngör, Struct. Chem. 19 (2008) 879.
- [37] G.S. Kürkçüoğlu, O.Z. Yeşilel, I. Çaylı, O. Büyükgüngör, Z. Kristallog. 224 (2009) 493.
- [38] G.S. Kürkçüoğlu, O.Z. Yeşilel, I. Kavlak, O. Büyükgüngör, J. Mol. Struct. 920 (2009) 220.
- [39] V.M. Nikitina, O.V. Nesterova, V.N. Kokozay, V.V. Dyakonenko, O.V. Shishkin, J. Jezierska, Polyhedron 28 (2009) 1265.
- [40] I. Potocnak, M. Vavra, E. Cizmar, K. Tibenska, A. Orendacova, D. Steinborn, C. Wagner, M. Dusek, K. Fejfarova, H. Schmidt, T. Muller, M. Orendac, A. Feher, J. Sol. State Chem. 179 (2006) 1965.
- [41] J. Kuchar, J. Cernak, K.A. Abboud, Acta Crystallogr. C 60 (2004) M492.

- [42] J. Kuchar, J. Cernak, Z. Mayerova, P. Kubacek, Z. Zak, Sol. St. Phen. 90-91 (2003) 323.
- [43] C.J. Shorrock, H. Jong, R.J. Batchelor, D.B. Leznoff, Inorg. Chem. 42 (2003) 3917.
- [44] Z. Smekal, I. Cisarova, J. Mrozinski, Polyhedron 20 (2001) 3301.
- [45] D.K. Venetopoulou, K.G. Keramidas, G.P. Voutsas, P.I. Rentzeperis, K. Goubitz, C. Tsiamis, Z. Kristallog. 209 (1994) 170.
- [46] G.S. Kürkçüoğlu, T. Hökelek, M. Aksel, O.Z. Yeşilel, H. Dal, J. Inorg. Organomet. Poly. Mat. 21 (2011) 602.
- [47] M. Aksel, Kürkçüoğlu G.S., Yeşilel O.Z., Büyükgüngör O., J. Mol. Struct. 1059 (2014)101.
- [48] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. A 64 (2008) 112.
- [49] Stoe & Cie (2002) X-AREA (Version 1.18), Darmstadt, Germany, (2002).
- [50] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M.
- Towler, J. van De Streek, J. Appl. Crystallogr. 2006, 39, 453-457
- [51] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
- [52] X.F. Shan, L.Z. Wu, X.Y. Liu, L.P. Zhang, C.H. Tung, Eur. J. Inorg. Chem. (2007) 3315.
- [53] A. Mukhopadhyay, S. Pal, Eur. J. Inorg. Chem. (2006) 4879.
- [54] G.S. Kürkçüoğlu, O.Z. Yeşilel, I. Çaylı, O. Büyükgüngör, J. Mol. Struct. 994 (2011) 39.
- [55] V. Gutmann, G. Resch, Coord. Chem. Rev. 43 (1982) 133.
- [56] T.N. Fedotova, G.G. Aleksandrov, G.N. Kuznetsova, Russ. J. Inorg. Chem. 56 (2011) 698.
- [57] M.G. Giorgini, M.R. Pelletti, G. Paliani, R.S. Cataliotti, J. Raman Spectrosc. 14 (1983)16.
- [58] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination compounds, J.Wiley and Sons, New York 1997.
- [59] R.L. McCullough, L. Jones, G. Crosby, Spectr. Acta 16 (1960) 929.

- [60] L.H. Jones, Inorg. vibrational spectroscopy, Marcel Dekker, New York,, 1971..
- [61] K. Nakamoto, J. Mol. Struct. 408 (1997) 11. Accepter

Complexes	1	2	3	4	
Empirical formula	$C_{48}H_{96}N_{32}Ni_4Zn_4$	$C_{12}H_{24}N_8NiCd\\$	$C_{12}H_{24}N_8PdZn$	C ₁₂ H ₂₄ N ₈ PdCd	
Formula weight	1617.88	451.50	452.16	499.19	
Crystal system	Tetragonal	Tetragonal	Orthorhombic	Monoclinic	
Space group	$I4_1/a$	I4 ₁ /a	Pbca	P21/c	
<i>a</i> (Å)	12.9907(4)	13.2594(2)	10.0976(5)	6.8223(6)	
<i>b</i> (Å)	12.9907(4)	13.2594(2)	12.7033(9)	14.6538(9)	
<i>c</i> (Å)	45.8775(19)	46.6030(12)	13.9812(7)	10.5120(9)	
β(°)	90.00	90.00	90.00	120.671(6)	
$V(\text{\AA}^3)$	7742.2(6)	8193.4(3)	1793.41(18)	903.90(14)	
Ζ	4	16	4	2	
$\mu (\mathrm{mm}^{-1})$	2.22	1.96	2.35	2.18	
$D_{\rm calc}$ (Mg m ⁻³)	1.388	1.464	1.675	1.834	
Crystal size (mm)	0.32×0.19×0.11	0.62×0.45×0.34	0.26 ×0.19×0.13	0.76×0.45×0.23	
θ Range (°)	1.6-26.2	1.6-26.2	1.5-28.0	2.3-27.9	
Measured reflections	27938	28212	12656	13039	
Independent reflections	3873	4099	1863	1878	
R _{int}	0.069	0.040	0.054	0.031	
$R[F^2 > 2\sigma(F^2)], wR(F^2)$	0.072-0.192	0.048-0.146	0.046-0.166	0.023-0.047	
Goodness-of-fit on F^2	1.14	1.02	1.13	1.11	
$\Delta \rho_{\rm max}$ (e Å ⁻³)	0.62	0.77	1.29	0.55	
$\Delta \rho_{\min} (e \text{ Å}^{-3})$	- 0.56	-0.57	-1.39	-0.30	

ſ

Table 1.	Crystal	lographic o	lata and s	structure	refinement	parameters	for com	plexes 1	L-4.
----------	---------	-------------	------------	-----------	------------	------------	---------	----------	------

Complex 1	Complex 1 Complex 2							
Bond Lengths	s (Å)				Bond Le	ngths (Å)		
C1-Ni1	1.843(10)	N3-Zn1 ⁱ	2.152(7)	C1-Ni1	1.855(9)	N2-Cd1	2.320(6)	
C2-Ni1	1.861(9)	N5-Zn1	2.193(10)	C2-Ni1	1.852(8)	N5-Cd1	2.319(11)	
C3-Ni1	1.841(8)	N6-Zn1	2.172(12)	C3-Ni1	1.844(11)	N6-Cd1	2.330(11)	
C4-Ni1	1.853(10)	N7-Zn1	2.213(11)	C4-Ni1	1.846(9)	N7-Cd1	2.382(12)	
N2-Zn1	2.100(8)	N8-Zn1	2.131(10)	N1-Cd1	2.287(7)	N8-Cd1	2.352(14)	
Angles (°)					Angl	es (°)		
C3-Ni1-C1	175.9(5)	N3 ⁱⁱ -Zn1-N6	85.2(4)	C3-Ni1-C4	90.2(5)	N2-Cd1-N6	165.0(4)	
C3-Ni1-C4	86.5(4)	N2-Zn1-N5	89.8(4)	C3-Ni1-C2	88.9(4)	N1-Cd1-N8	170.1(5)	
C1-Ni1-C4	91.9(5)	N8-Zn1-N5	100.6(5)	C4-Ni1-C2	179.0(5)	N5-Cd1-N8	91.0(4)	
C3-Ni1-C2	91.8(3)	N3 ⁱⁱ -Zn1-N5	91.5(4)	C3-Ni1-C1	179.7(6)	N2-Cd1-N8	82.8(4)	
C1-Ni1-C2	89.6(5)	N6-Zn1-N5	87.2(5)	C4-Ni1-C1	89.6(5)	N6-Cd1-N8	96.7(5)	
C4-Ni1-C2	178.0(5)	N2-Zn1-N7	91.8(4)	C2-Ni1-C1	91.3(3)	N1-Cd1-N7	89.7(4)	
N2-Zn1-N8	92.8(4)	N8-Zn1-N7	79.7(5)	N1-Cd1-N5	95.4(4)	N5-Cd1-N7	174.7(4)	
N2-Zn1-N3 ⁱⁱ	89.9(3)	N3 ⁱⁱ -Zn1-N7	88.1(4)	N1-Cd1-N2	89.9(3)	N2-Cd1-N7	92.9(4)	
N8-Zn1-N3 ⁱⁱ	167.6(4)	N6-Zn1-N7	91.1(5)	N5-Cd1-N2	88.4(4)	N6-Cd1-N7	102.0(5)	
N2-Zn1-N6	174.2(4)	N5-Zn1-N7	178.3(5)	N1-Cd1-N6	92.1(4)	N8-Cd1-N7	84.0(5)	
N8-Zn1-N6	92.6(5)			N5-Cd1-N6	76.6(5)			
Symmetry co -y+3/4, $-z+7$	Symmetry code	Symmetry codes: (i) $x-3/4$, $-y+5/4$, $-z+5/4$; (ii) $-x+5/4$, $y+3/4$, $-z+5/4$						
Complex 3					Comp	lex 4		
Bond Lengths	s (Å)				Bond Len	gths (Å)		
Pd1-N1	2.301(3)	Pd2-C5	1.990(3)	N1-Cd1	2.293(3)	Pd1-C1 ⁱ	1.989(3)	
Pd1-N2	2.377(3)	Pd2-C6	1.996(4)	N2-Cd1	2.379(2)	Pd1-C2 ⁱ	2.001(3)	
Pd1-N3	2.426(3)			N3-Cd1	2.433(2)			
Angles (°)				Angles (°)				
N1 ⁱ -Pd1-N2	101.78(10)	N2-Pd1-N3	87.86(10)	C1-Pd1-C2 ⁱ	90.54(11)	N1-Cd1-N2 ⁱⁱ	101.80(8)	
N1 ⁱ -Pd1-N2 ⁱ	78.22(10)	N2-Pd1-N3	ⁱ 92.14(10)	C1i-Pd1-C2 ⁱ	89.46(11)	N1-Cd1-N3	89.26(8)	
N1-Pd1-N3	89.30(11)	C5-Pd2-C6	ⁱⁱ 90.65(13)	N3-C1-Pd1	177.40(3)	N1 ⁱⁱ -Cd1-N3	90.74(8)	
N1 ⁱ -Pd1-N3	90.70(11)	C5 ⁱⁱ -Pd2-C6 ⁱ	ⁱ 89.35(13)	N4-C2-Pd1	179.20(3)	N2-Cd1-N3	87.83(8)	
				N1-Cd1-N2	78.20(8)	N2-Cd1-N3 ⁱⁱ	92.17(8)	
Symmetry council $-z+2$.	des: (i) -x+1,	-y+1, -z+1; (ii) -x+1, -y+1,	Symmetry code $-z+1$.	es: (i) -x+1, -	-y+1, -z+2; (ii)	-x+1, -y+1,	

Table 2. Selected bond distances (Å) and angles (°) for the complexes.

Figure Captions

Fig. 1. The view of the octanuclear cubane-like structure of complexes 1 or 2 (some H atoms are omitted for clarity, (i) 1-x, ¹/₂-y, z; (ii) -¹/₄+x, ³/₄-y 1.75-z; (iii) ³/₄-x, ¹/₄+y, 1.75-z)

Fig. 2. The 2D hydrogen-bonded layer in 1 or 2.

Fig. 3. The 3D hydrogen-bonded network in 1 or 2.

Fig. 4. The asymmetrical unit and the view of the one-dimensional structure of complex 4 (all

JUS

H atoms are omitted for clarity).

Fig. 5. The unit cell in 4.

CCE

Fig. S1. The FT-IR spectra of the complexes.

Fig. S2. The Raman spectra of the complexes.

Fig. S3. The TG, DTG and DTA curves of 1.

Fig. S4. The TG, DTG and DTA curves of 2.

Fig. S5. The TG, DTG and DTA curves of 3.

Fig. S6. The TG, DTG and DTA curves of 4.



Fig. 1. The view of the octanuclear cubane-like structure of complexes **1** or **2** (some H atoms are omitted for clarity, (i) 1-x, ¹/₂-y, z; (ii) -¹/₄+x, ³/₄-y 1.75-z; (iii) ³/₄-x, ¹/₄+y, 1.75-z)



Fig. 2. The 2D hydrogen-bonded layer in 1 or 2.



Fig. 3. The 3D hydrogen-bonded network in 1 or 2.

en-bonk



Fig. 4. The asymmetrical unit and the view of the one-dimensional structure of complex 4 (all

H atoms are omitted for clarity).



Fig. 5. The 2D hydrogen-bonded layer in 4.



Herein we report on a series of complexes containing dmen (dmen = N,Ndimethylethylenediamine) units and cyano groups, namely bimetallic octanuclear and binuclear $[Zn_4(dmen)_8Ni_4(CN)_{16}]$, $[Cd_4(dmen)_8Ni_4(CN)_{16}]$, $[Zn(dmen)_2Pd(\mu-CN)_2(CN)_2]$ and tetracyanonickelate(II) $[Cd(dmen)_2Pd(\mu-CN)_2(CN)_2].$ result of using or As a tetracyanopalladate(II) complexes, different structural complexes have been obtained. When Zn(II) and Cd(II) ions are used, the complexes obtained with tetracyanonickelate(II) exhibit a cubic structure, whilst the complexes obtained with tetracyanopalladate(II) have a 1D polynuclear structure. The reason for this difference is thought to arise from the strong C-H...Ni interactions between the methyl groups and the Ni(II) metal with a small radius.