Inorg. Chem. **2005**, *44*, 217−224

Inorganic Chemistry
Article

Knotted Network Consisting of 3-Threads and a Zwitterionic One-Dimensional Polymorphs of *trans*-3-(3-Pyridyl)acrylate of Cobalt and Nickel, $M^{II}(C_8H_6NO_2)_2(H_2O)_2$

Mohamedally Kurmoo,[*,†] Claude Estournès,[○,#] Yoshimi Oka,[‡,§] Hitoshi Kumagai,[§] and Katsuya Inoue[§,‖]

Laboratoire de Chimie de Coordination Organique, CNRS-UMR7140, Université Louis Pasteur, 4 rue Blaise Pascal, F-67000 Strasbourg Cedex, France, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR7504-CNRS-ULP, 23 rue du Loess, 67034 Strabourg Cedex2, France, Graduate University for Advanced Studies, Institute of Molecular Science, Nishigouanaka 38, Myoudaiji, Okazaki, Aichi 444-8585, Japan, Institute of Molecular Science, Nishigouanaka 38, Myoudaiji, Okazaki, Aichi 444-8585, Japan, and Department of Chemistry, Faculty of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi Hiroshima, Hiroshima 739-8526, Japan

Received August 20, 2004

We present the hydrothermal synthesis, characterization (IR, DT-TGA), single-crystal structures, and magnetic properties of two polymorphs of *trans*-3(3-pyridyl)acrylate of cobalt(II) and of nickel(II), $M^{II}(C_8H_6NO_2)_2(H_2O)_2$. Hydrothermal reaction at 120 or 170 °C results exclusively in the different polymorphs. The infrared spectra and thermogravimetric analyses of the complexes are almost similar for the two polymorphs but show a difference between cobalt and nickel in energies of the vibrational modes and in the decomposition temperatures. The crystal structures of the two polymorphs are quite different; one crystallizes in a monoclinic space group and the other in a triclinic. This major difference is due to the different stereochemistry, *cis* or *trans*, of the coordination at the metal sites. When it is *trans*-MN_2O_4, it results in the monoclinic cell consisting of a 3D-network of metals bridged by the ligands through single bonds (M–N and M–O). There is threading of three sublattices up to $2a \times 4b \times 2c$, at which point the three sublattices are knotted into one infinite framework. When it is *cis*-MN_2O_4, it results in the triclinic cell and consists of Zwitterionic linear chains of metals bridged by one single ligand via the pyridine and a bidentate carboxylate group and the other ligand is bonded only via the pyridine while its carboxylate end is free. All four compounds are paramagnetic with Weiss constants suggesting weak interactions.

Introduction

The field of coordination chemistry has had a great boost in the last 20 years with the design of novel materials by use of the secondary coordination of designed ligands whose binding sites are placed at distances preventing them from chelating.[1,2] It is now possible to predict, in some cases, the structural propagation by use of these designed ligands with specific coordinating groups and geometry.[3] Such ligands

---

[*] To whom correspondence should be addressed. E-mail: kurmoo@chimie.u-strasbg.fr. Phone: +33 3 90 24 13 56. Fax: +33 3 90 24 13 25.

[†] Laboratoire de Chimie de Coordination Organique.

[○] Institut de Physique et Chimie des Matériaux de Strasbourg.

[#] Present address: Plate-forme Nationale de Frittage Flash, CIRIMAT, UMR5085 CNRS, Université Paul Sabatier, 118 route de Narbonne 31062 Toulouse Cedex 04, France. E-mail: estourne@chimie.ups-tlse.fr.

[‡] Graduate University for Advanced Studies, Okazaki.

[§] Institute of Molecular Science, Okazaki.

[‖] Department of Chemistry, Faculty of Science, Hiroshima University.

(1) (a) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, 1995. (b) Lehn, J.-M. *Chem. Eur. J.* **2000**, *6*, 2097.

(2) (a) Special issue on Structure, Properties and Applications of Inorganic Polymers: *Coord. Chem. Rev.* **2003**, *246*, 1−353. (b) *Molecular Self-assembly, Organic versus inorganic approaches, Structure and Bonding*; Fujita, M., Ed.; Springer-Verlag: Berlin, 2000, Vol. 96. (c) Special issue on Molecular Networks: Hosseini, M. W., Ed. *New J. Chem.* **1998**, *22*. (d) *Molecular Catenanes, Rotaxanes and Knots: A Journey Through the World of Molecular Topology*; Sauvage, J.-P., Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, 1999. (e) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (f) *Transition Metals in Supramolecular Chemistry*; Beer, P. D., Ed.; Kluwer: Dordrecht, 1994. (g) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. (h) Forster, P. M.; Cheetham, A. K. *Top. Catal.* **2003**, *24*, 79−86. (i) Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289. (j) Robson, R. *J. Chem. Soc., Dalton. Trans.* **2000**, 3735. (k) Janiak, C. *J. Chem. Soc., Dalton. Trans.* **2003**, 2781. (l) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.

(3) Lehn, J.-M. *Rep. Prog. Phys.* **2004**, *67*, 249.

10.1021/ic0488536 CCC: $30.25

are known as polytopic, and the smallest and simplest of such ligands is the cyanide ion.[4] It is also described as ambidentate due to the possible coordination by both carbon and nitrogen, and in this particular case, the ligand field is very strong when it is carbon bonded and weak when it is nitrogen bonded. Extended networks made with cyanide bridges are numerous and have been known for a long time, in particular, the Prussian blue family now enjoying a renaissance due to its interesting and tunable magnetic properties depending on the choice of metal, oxidation state, and counterions. The dual crystal-field strength of the cyanide ion is the key to the range of optical, electrical, magnetic, and magneto-optical effects observed.[5] Examples of other small anionic ligands that play similar structural role, but without the dual ligand-field effect, are nitrate, nitrite, thiocyanate, carbonate, sulfate, and azide while larger ones are the polycyanides such as dicyanamide (dca),[6] tricyanomethanide (tcm),[7] tetracyanoethylene (tcne),[8] tetracyanoquinodimethane (tcnq),[9] and *N*,*N′*-dicyanobenzoquinonediimine (dcnqi).[10] However, the most active development in coordination network chemistry lies in the use of polypyridine,[11] polycarboxylate,[12] polyphosphate,[13] and also polyalcohol.[14] Combining these ligands to generate infinite lattices with programmed structures is a fast growing field of research, and much of it has been reviewed.[2]

From a physical chemistry point of view, several aspects of these coordination compounds are of interest, viz., their collective property such as magnetism,[15] the porosity and the surface of the pores,[16] and the optical properties[17] associated with nonlinear activity in addition to the luminescence of the metals and/or ligands. More recently, the idea of synthesizing compounds with stable porosity and displaying long-range magnetic ordering has been realized.[18] The specific sensitivity of these porous compounds to different solvents opens new ventures in the fabrication of sensors. It has to be noted here that among the most successful and commonly used ligands for magnetism, in recent years, are the polycarboxylate and polycyanide. These have generated a wide range of compounds with interesting chemistry and physical properties. For the polycarboxylate, it has been shown that the temperature of the hydrothermal reaction can be the principal factor determining the production of specific phase. For example, the reaction of succinate ($C_4H_4O_4^{2-}$) with cobalt(II) produces different compounds,[19] where the number of coordinated water molecules appears to decrease as the reaction temperature is increased. It has also been demonstrated that the pore size can be tuned by choosing the dicarboxylate unit with an appropriate size.[20] On the other hand, increasing the number of carboxylate group attached to a benzene ring can increase the number of metal ions coordinated to it, renders these ligands as scavengers of metal ions, and can be of great use in environmental purification.[21] For example, the pyromellitate tetra-anion can have up to 12 cobalt centers attached to it. These possibilities are due to the range of coordination

---

(4) (a) Verdaguer, M.; Bleuzen, A.; Train, C.; Garde, R.; Fabrizi de Biani, F.; Desplanches, C. *Philos. Trans. R. Soc. London, Ser. A* **1999**, *357*, 2959. (b) Ohba, M.; Okawa, H. *Coord. Chem. Rev.* **2002**, *198*, 313. (c) Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2110.

(5) (a) Ikeda, K.; Ohkoshi, S.-I.; Hashimoto, K. *Electrochemistry* **2003**, *71*, 184. (b) Ikeda, K.; Ohkoshi, S.-I.; Hashimoto, K. *J. Appl. Phys.* **2003**, *93*, 1371. (c) Ohkoshi, S.-I.; Abe, Y.; Fujishima, A.; Hashimoto, K. *Phys. Rev. Lett.* **1999**, *82*, 1285.

(6) (a) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103. (b) Kurmoo, M.; Kepert, C. J. *New J. Chem.* **1998**, *22*, 1515.

(7) (a) Batten, S. R.; Hoskins, B. F.; Robson, R. *Chem. Eur. J.* **2000**, *6*, 156. (b) Jensen, P.; Price, D. J.; Batten, S. R.; Moubaraki, B.; Murray, K. S. *Chem. Eur. J.* **2000**, *6*, 3186. (c) Kurmoo, M. *Mol. Cryst. Liq. Cryst.* **2000**, *342*, 167.

(8) (a) Miller, J. S. *Inorg. Chem.* **2000**, *39*, 4392. (b) Falk, K.; Balanda, M.; Tomkowicz, Z.; Mascarenhas, F.; Schilling, J.; Klavins, P.; Haase, W. *Polyhedron* **2001**, *20*, 1521.

(9) (a) Clérac, R.; O'Kane, S.; Cowen, J.; Ouyang, X.; Heintz, R.; Zhao, H.; Bazile, M. J., Jr.; Dunbar, K. R. *Chem. Mater.* **2003**, *15*, 1840. (b) Zhao, H.; Heintz, R. A.; Dunbar, K. R.; Rogers, R. D. *J. Am. Chem. Soc.* **1996**, *118*, 12844. (c) Zhao, H.; Bazile, M. J., Jr.; Galán-Mascarós, J. R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1015.

(10) Kato, R. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 515.

(11) (a) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (b) Moulton, B.; Zaworotko, M. J. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 117−123. (c) Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, *236*, 91. (d) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 5158. (e) Kitagawa, S.; Masaoka, S. *Coord. Chem. Rev.* **2003**, *246*, 73.

(12) (a) Mehrothra, R. C.; Bhora, R. *Metal Carboxylates*; Academic Press: New York, 1983. (b) Oldham, C. *Prog. Inorg. Chem.* **1968**, *10*, 223. (c) Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209. (d) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633. (e) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3. (f) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (g) Cheetham, A. K.; Ferey G.; Loiseau, T. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3268.

(13) (a) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 268. (b) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125. (c) Clearfield, A. *Prog. Inorg. Chem.* **1998**, *47*, 371. (d) Cao, G.; Hong, H.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420. (e) Gavin, J. A. *Acc. Chem. Res.* **1998**, *31*, 209. (f) Clearfield, A. *Chem. Mater.* **1992**, *4*, 756. (g) Galarneau, A.; Barodawalla, A.; Pinnavaia, T. J. *Nature* **1995**, *374*, 529. (h) Rao, C. N. R.; Natarajan, S.; Choudhury, A.; Neeraj, S.; Ayi, A. A. *Acc. Chem. Res.* **2000**, *34*, 80. (i) Scott, B. J.; Wirnsberger, G.; Stucky, G. *J. Phys. Chem. B* **2002**, *106*, 2552.

(14) (a) Kitagawa, S.; Kawata, S. *Coord. Chem. Rev.* **2002**, *224*, 11. (b) Oh, M.; Carpenter, G. B.; Sweigart, D. A. *Acc. Chem. Res.* **2004**, *37*, 1.

(15) (a) Day, P. *J. Chem. Soc., Dalton Trans.* **2000**, 3483. (b) Issue on Metal-Organic and Organic Molecular Magnets: Day, P.; Underhill, A. E.; Eds. *Philos. Trans. R. Soc.* **1999**, *357*. (c) Kahn, O. *Acc. Chem. Res.* **2000**, *33*, 647. (d) *Molecular Magnetism, New Magnetic Materials*; Itoh; K., Kinoshita, M., Eds.; Gordon Breach-Kodansha: Tokyo, 2000. (e) Kurmoo, M. *Chem. Mater.* **1999**, *11*, 3370. (f) Kurmoo, M. *Philos. Trans. R. Soc. London, Ser. A* **1999**, *357*, 3041. (g) Kurmoo, M.; Kumagai, H.; Hughes, S. M.; Kepert, C. J. *Inorg. Chem.* **2003**, *42*, 6709. (h) Blundell, S. J.; Pratt, F. L. *J. Phys. Condens. Matter* **2004**, *16*, R771.

(16) (a) Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739. (b) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1999**, 375. (c) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Solid State Chem.* **2000**, *152*, 261. (c) Maspoch, D.; Ruiz-Molina, D.; Wurst, K.; Domingo, N.; Cavallini, M.; Biscarini, F.; Tejada, J.; Rovira, C.; Veciana, J. *Nat. Mater.* **2003**, *2*, 190.

(17) (a) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511 and references therein. (b) Evans, O. R.; Lin, W. *Chem. Mater.* **2001**, *13*, 2705.

(18) (a) Rujiwatra, A.; Kepert, C. J.; Claridge, J. B.; Rosseinsky, M. J.; Kumagai, H.; Kurmoo, M. *J. Am. Chem. Soc.* **2001**, *123*, 10584. (b) Yang, X. D.; Si, L.; Ding, J.; Ranford, J. D.; Vittal, J. J. *Appl. Phys. Lett.* **2001**, *78*, 3502. (c) Ranford, J. D.; Vittal, J. J.; Wu, D. Q.; Yang, X. D. *Angew. Chem., Int. Ed.* **1999**, *38*, 3498. (d) Zhang, X. X.; Chui, S. S. Y.; Williams, I. D. *J. Appl. Phys.* **2000**, *87*, 6007. (e) Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 12096. (f) Wang, Z.; Zhang, B.; Fujiwara, H.; Kobayashi, H.; Kurmoo, M. *Chem. Commun.* **2004**, 416.

(19) Forster, P. M.; Burbank, A. R.; Livage, C.; Férey, G.; Cheetham, A. K. *Chem. Commun.* **2004**, 368.

(20) Li, H.; Eddouadi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.

geometries of each carboxylate unit, viz., mono-, bi-, and tridentate and *syn*–*syn*, *syn*–*anti*, and *anti*–*anti* modes, and furthermore, it can be chelating as well as bridging.[12] From a magnetic point of view, the carboxylate metal complexes are more interesting as a consequence of the range of coordination modes as well as for the fact that the carboxylate group can bring the metal centers closer to one another, through M–O–M and M–O–C–O–M bridges, to generate clusters, infinite chains, two-dimensional layers and three-dimensional frameworks, having strong exchange magnetic interactions between nearest neighbors. In contrast, the range of coordination of polycyanide is limited; while it is easier to predict the structures of the final products, they form very few long-ranged ordered magnets. Although polypyridine ligands are the most studied in the field of coordination polymers, they rarely provide interesting magnetic materials, due to their bulkiness.[11]

Fused ligands containing pyridine and carboxylate groups have been the subject of many studies, in particular for their porosity and nonlinear optical activity.[17,22,23] Early works with nicotinate and isonicotinate have been extended to other pyridine- and bipyridine-carboxylate or -dicarboxylate. Interestingly, several phases have been identified in most cases depending on the synthetic procedure applied.

Following our work on cinnamate and carboxycinnamate and also on α-hydroxy- and α-amino-phenylacetate where we have shown the existence of square-grid cobalt carboxylate layers with M–O–C–O-M bridges either connected or not, depending on the ligand, we have now undertaken a similar study where the benzene moiety of the cinnamate is replaced by a pyridine, *trans*-3(3-pyridyl)acrylate.[24] There are several reasons for this study, and they are the following: (a) there are two sterically hindered positions possible which may introduce polymorphism, (b) there is competition between N and O bonding to the metals, (c) the ligand can be di-, tri-, or tetratopic to generate a polymeric network, and (d) the ligand has a permanent electric dipole which may give rise to nonlinear optical activity. This slight chemical change, by replacing the benzene by pyridine, has a severe consequence on the structures due to the extra bonding ability of the ligand through the pyridine. Coordination compounds of *trans*-3(4-pyridyl)acrylate[25] (4-pyac) of divalent Cd, Zn, Ni, Co, Cu are known, and that of Cu with *trans*-3(2-pyridyl)acrylate[26] (2-pyac) has been described. In general, these compounds form polymers of an interpenetrating diamond network where the number of interpenetrating lattices depends on the metal, the ligands, the other coordinating ligands, and the solvents. With *trans*-3(3-pyridyl)-acrylate[27] (3-pyac), only three complexes exist, [Zn(OH)(3-pyac)], $[Co_2(\mu\text{-}H_2O)(3\text{-pyac})_4]\cdot 3\text{-pyacH}\cdot 2H_2O$, and $[Ni_2(\mu\text{-}H_2O)(3\text{-pyac})_4]\cdot 3\text{-pyacH}\cdot H_2O$, and all three have polymeric structures. Here, we report the single crystal structures of two new polymeric modifications of cobalt and nickel with *trans*-3(3-pyridyl)acrylate, selectively prepared by a hydrothermal technique, and their thermal and magnetic properties.

Experimental Section

Materials. All reagent grade chemicals were obtained from Fluka or Aldrich and were used without further purification. Distilled water was used throughout.

Preparation of Compounds. The compounds were prepared by hydrothermal technique in autoclaves of 120 mL capacity with Teflon linings. *trans*-3(3-Pyridyl)acrylic acid (3 mmol) was first neutralized with NaOH (3 mmol) to give a clear solution to which the hexaaquo-metalate(II)-dichloride (6 mmol) was added and stirred to give a homogeneous suspension. The mixture is then placed in the autoclave, filled with water to three-quarters capacity, sealed, and heated at either 120 or 170 °C for 3 days. They were then quench-cooled in a water bath.

The reactions at 120 °C gave orange-red block crystals in a clear red solution for cobalt and blue-green crystals in a light green solution for nickel. In both cases, the yield is more than 90% based on the acid. The reactions at 170 °C gave small dark red crystals with some cobalt-oxides in a red solution for cobalt and large transparent green crystals in a clear green solution for nickel. The yield is only 70% for the nickel compound and 30% for the cobalt compound. For convenience, we will label them as **Co120**, **Ni120**, **Co170**, and **Ni170**, respectively.

Anal. Calcd for **Co120**, $C_{16}H_{16}CoN_2O_6$: C, 49.12; H, 4.12; N, 7.16. Found: C, 49.0; H, 4.3, N 7.2%. Calcd for **Co170**, $C_{16}H_{16}CoN_2O_6$: C, 49.12, H 4.12, N 7.16. Found: C, 49.3; H, 4.3; N, 7.1%. Calcd for **Ni120**, $C_{16}H_{16}NiN_2O_6$: C, 49.15; H, 4.12; N, 7.16. Found: C, 49.6; H, 4.0; N, 7.3%. Calcd for **Ni170**, $C_{16}H_{16}NiN_2O_6$: C, 49.15, H, 4.12; N, 7.2. Found: C, 49.1; H, 4.5; N, 7.2%.

Infrared (ν/cm^{-1}, 400–4000 cm^{-1}) spectra: **Co120**, 3315, 3235, 3070, 3010, 2812, 1643, 1548, 1480, 1423, 1385, 1372, 1335, 1300, 1258, 1208, 1182, 1126, 1100, 1052, 1034, 974, 928, 880, 862, 810, 726, 698, 646, 602; **Ni120**, 3330, 3258, 3072, 2796, 1642, 1540, 1480, 1422, 1386, 1372, 1338, 1300, 1260, 1182, 1126, 1100, 1054, 1035, 990, 974, 934, 904, 878, 864, 810, 754, 730, 700, 644, 616, 600; **Co170**, 3378, 3250, 1642, 1544, 1481, 1408, 1362, 1096, 978, 884, 910, 750, 718, 688, 644, 606; **Ni170**, 3330, 3275, 2788, 1644, 1546, 1482, 1424, 1388, 1372, 1336, 1300, 1262, 1212, 1182, 1126, 1098, 992, 974, 934, 906, 878, 864, 810, 754, 732, 698, 648, 614, 602.

---

(21) (a) Kumagai, H.; Kepert, C. J.; Kurmoo, M. *Inorg. Chem.* **2002**, *41*, 3410 and references therein. (b) Snejko, N.; Gutierrez-Puebla, E.; Martinez, J. L.; Monge, M. A.; Ruiz-Valero, C. *Chem. Mater.* **2002**, *14*, 1879. (c) Kumagai, H.; Chapmann, K. M.; Kepert, C. J.; Kurmoo, M. *Polyhedron* **2003**, *22*, 1921.

(22) (a) Batten, S. R. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 107. (b) Schareina, T.; Schick, C.; Kempe, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 131. (c) Liu, Y.-H.; Lu, Y.-L.; Wu, H.-C.; Wang, J.-C.; Lu, K.-L. *Inorg. Chem.* **2002**, *41*, 2592. (d) Tynan, E.; Jensen, P.; Kruger, P. E.; Lees, A. C.; Nieuwenhuyzen, M. *J. Chem. Soc., Dalton Trans.* **2003**, 1223.

(23) (a) Ayyappan, P.; Evans, O. R.; Lin, W. *Inorg. Chem.* **2001**, *40*, 4627–4632. (b) Lu, J. Y.; Babb, A. M. *Chem. Commun.* **2002**, 1340. (c) Lu, J. Y.; Babb, A. M. *Chem. Commun.* **2001**, 821.

(24) (a) Kumagai, H.; Oka, Y.; Inoue, K.; Kurmoo, M. *J. Chem. Soc., Dalton Trans.* **2002**, 3442. (b) Kumagai, H.; Oka, Y.; Inoue, K. Kurmoo, M. *J. Phys. Chem. Solids* **2003**, *65*, 55.

(25) (a) Zhang, J.; Lin, W.; Chen, Z.-F.; Xiong, R.-G.; Abrahams, B. F.; Fun, H.-K. *J. Chem. Soc., Dalton Trans.* **2001**, 1806. (b) Wang, X.-S.; Zhao, H.; Qu, Z.-R.; Ye, Q.; Zhang, J.; Xiong, R.-G.; You, X.-Z.; Fun, H.-K. *Inorg. Chem.* **2003**, *42*, 5786. (c) Liu, Y.-H.; Lin, C.-S.; Chen, S.-Y.; Tsai, H.-L.; Ueng, C.-H.; Lu, K.-L. *J. Solid State Chem.* **2001**, *157*, 166.

(26) Zhao, H.; Qu, Z.-R.; Ye, Q.; Wang, X.-S.; Zhang, J.; Xiong, R.-G.; You, X.-Z. *Inorg. Chem.* **2004**, *43*, 1813.

(27) (a) Zhou, Q.-X.; Wang, Y.-J.; Zhao, X.-Q.; Yue, L. *Chin. J. Inorg. Chem.* **2004**, *19*, 1245. (b) Qu, Z.-R.; Zhao, H.; Wang, Y.-P.; Wang, X.-S.; Ye, Q.; Li, Y.-H.; Xiong, R.-G.; Abrahams, B. F.; Liu, Z.-G.; Xue, Z.-L.; You, X.-Z. *Chem. Eur. J.* **2004**, *10*, 53.

Table 1. Crystal Data and Summary of Structure Refinement for the Four Compounds

	Co120	Co170	Ni120	Ni170
empirical formula	$C_{16}H_{16}CoN_2O_6$	$C_{16}H_{16}CoN_2O_6$	$C_{16}H_{16}NiN_2O_6$	$C_{16}H_{16}NiN_2O_6$
fw	391.25	391.25	391.01	391.01
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group (No.)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a/Å	16.942(4)	7.620(1)	16.812(3)	7.657(8)
b/Å	5.461(2)	9.644(2)	5.443(1)	9.687(10)
c/Å	18.001(5)	11.978(2)	17.869(4)	12.04(1)
α/deg	90	66.552(3)	90	66.53(2)
β/deg	106.246(4)	81.306(2)	106.229(3)	81.18(2)
γ/deg	90	84.953(2)	90	84.64(2)
V/Å^3	1599.0(7)	797.8(2)	1569.9(5)	809(1)
Z	4	2	4	2
T/K	296	296	296	296
D(calcd)/g cm^{-3}	1.625	1.629	1.654	1.605
μ/cm^{-1}	1.111	1.113	1.274	1.236
λ(Mo Kα)/Å	0.71073	0.71073	0.71073	0.71073
reflns (total)	3611	3508	3504	2992
reflns_gt^a	2803	3255	1832	2992
threshold	$F^2 > 2.0\sigma(F^2)$	$F^2 > 2.0\sigma(F^2)$	$F^2 > 2.0\sigma(F^2)$	$F^2 > 2.0\sigma(F^2)$
$R1$	0.0438	0.0468	0.0648	0.0538
$wR2^b$	0.1223	0.1680	0.1828	0.1671
no. params	229	226	229	226
GOF on F^2	1.390	1.312	1.273	1.309
residual electron max/min (e Å^{-3})	0.56/−0.72	0.62/−0.62	1.35/−1.33	0.68/−0.65

^{a} gt = greater than the threshold which is $2\sigma(F^2)$. ^{b} $w = 1/[\sigma^2(F_o^2) + (0.05(\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3)^2]$; $1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.0P]$; $P = (F_o^2 + 2F_c^2)/3'$.

Analytical Procedures. Infrared data were collected on a Mattson FTIR spectrometer by transmission through samples deposited on a KBr crystal. Thermogravimetry and differential thermal analysis were performed on a TA apparatus at a warming rate of 4 °C per min in a constant flow of air. Magnetization measurements, as a function of temperature on cooling in field of 100 Oe and as a function of field at 2 K, were made on polycrystalline samples held in a gelatin capsule in a drinking straw.

X-ray Crystallography. Crystal data and final refinement parameters are summarized in Table 1. X-ray diffraction data collections were done on selected crystals glued to glass fibers by use of a Bruker CCD diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). All data were collected at room temperature (23 °C). Data were treated for absorption by SADABS[28] and analyzed by SAINT.[29] The structures were determined by direct methods using TEXSAN. All heavy atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were placed at ideal positions. The crystal and refinement data have been deposited at the Cambridge Crystallographic Data Centre and have been allocated the reference numbers 247653−247656.

Results and Discussion

Synthesis. Although the technique of hydrothermal synthesis has been proven to be very successful in the preparation of coordination polymers, it remains a very poorly understood technique in view of mechanism. Several trends have been highlighted, but these principally apply to the particular synthesis and are not generally applicable. Our observation of complete segregation of the two polymorphs by selecting the temperature of the reaction is fortuitous. As expected from previous work[22,23] on pyridyl-carboxylates, both the carboxylate and pyridine are coordinated to the metal. The **M170** complexes reported here are an exception with a free carboxylate group. However, the interesting and also expected difference is the total segregation of different phases in the crystallization/reaction process depending on the coordination stereochemistry at the metal sites. This also results in the different colors of the complexes; viz., blue green for the nickel compound with *trans*-pyridine and green for *cis*-pyridine while for the cobalt compounds it is orange red and dark red, respectively.

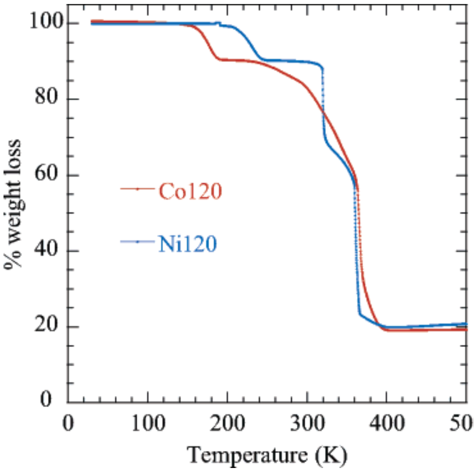


Figure 1. Traces of the thermogravimetric analyses of the nickel (blue) and cobalt (red) compounds prepared at 120 °C.

Infrared Spectroscopy. The infrared spectra of the complexes in the 400−4000 cm^{-1} range are dominated by the vibrational modes of the ligands and water molecules, and they are very similar to one another with some modes having marginally higher energies for the nickel complexes compared to the cobalt complexes. The symmetric and antisymmetric stretching modes of the coordinated water molecules are very broad and lie in the range 3100−3400 cm^{-1}. However, the bending mode is better defined and lies

---

(28) Blessings, R. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(29) *SMART, SAINT and XPREP. Area detector control and data integration and reduction software*; Bruker: Madison, WI, 1995.

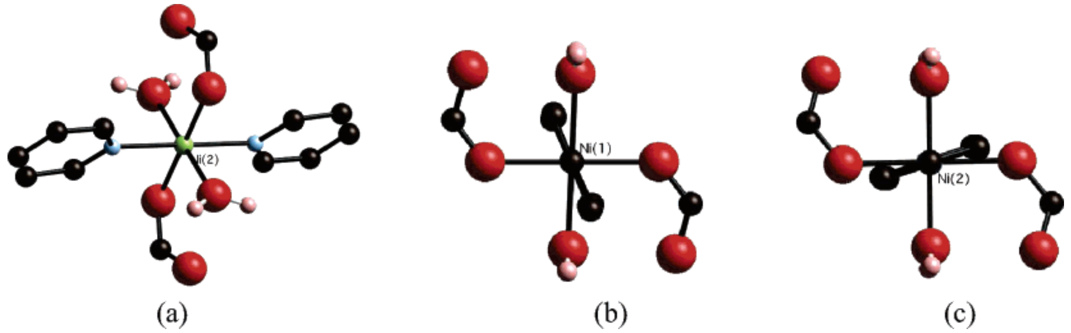


Figure 2. Coordination of the metal in the structures of **M120** compounds (a) and the different orientations of the pyridine ring for the two different observed metal sites (b and c).

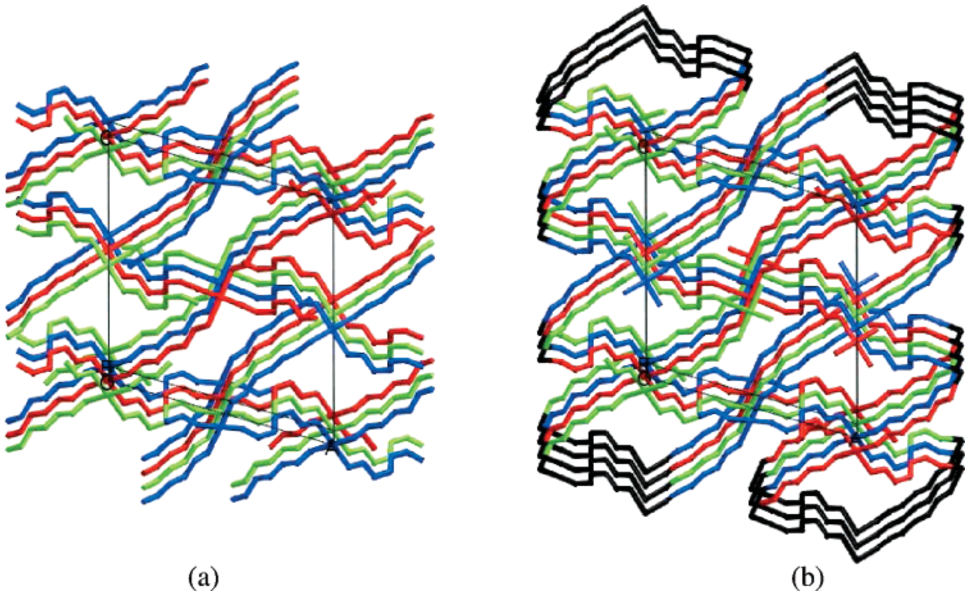


Figure 3. Structure of **M120**. (a) The three interlaced threads, represented in three colors, for an expansion of $<2a \times <4b \times <2c$. (b) The three lattices merge at the highlighted knots (in black) into one for an expansion beyond $>2a \times >4b \times >2c$.

at 1642 $\pm$ 2 cm^{-1}. The ligand bands belonging to the pyridyl ring and the carboxylate group can be separated from one another as the former gives rise to sharper peaks than the latter. They are also less intense. The symmetric and antisymmetric bands of the carboxylate group can, therefore, be assigned to the peak at 1544 $\pm$ 4 and 1367 $\pm$ 5 cm^{-1}, respectively. However, within the accuracy of the measurements ($\pm$4 cm^{-1}), it is difficult to point to any difference that may come from the different coordination modes and the uncoordinated carboxylate groups.[30]

Thermal Analysis. The traces of the thermogravimetric analyses of the **M120** compounds are shown in Figure 1; those of the **M170** compounds are similar. They are characterized by three weight losses until 500 °C in each case and by an additional one, in the case of cobalt, at 910 °C. The first loss amounts to 9.5% at 170 °C for cobalt and 215 °C for nickel, which is due to the loss of the coordinated water molecules (expected 9.2%). These losses are endothermic as expected. The second and third, which are better defined for the nickel compounds, are due to the combustion of the organic ligand and result in a mass of metal oxide of ca. 20%, Co_3O_4 for cobalt and NiO for nickel. Both of these are exothermic; the first generates less heat than the second. The last step for cobalt at 910 °C is due to the reduction of Co_3O_4 to CoO, amounts to 1.3% weight loss, and is in good agreement with the expected values and with the endothermic character. The first of the two steps for the combustion of the ligands in the case of nickel at 315 °C can be interpreted by the departure of CO_2 due to the decomposition of the carboxylate group, amounting to an expected loss of weight of 20% compared to that observed of ca. 22%. The second at 350 °C is the decomposition of the aromatic ring and the remaining carbon atoms into N_2 and CO_2. This is also in good agreement with the heat generated at the respective steps. This observation suggests that the bond strength of Ni$-$N is stronger than Ni$-$O. These steps are less well defined for the cobalt and may be interpreted as the bond strength being similar in this case. These interpretations are as expected from the coordination chemistry of the two metals as a consequence of their slightly different ionic radii.

Struture Analysis. The crystal structures of the compounds prepared at the two different temperatures are very different, but the complexes for the two metals prepared at

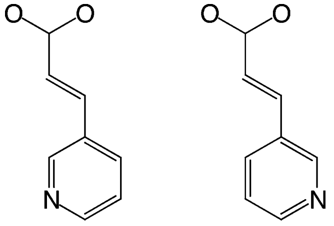
---

[30] (a) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; John Wiley and Sons: New York, 1997.

Table 2. Metal Ligand Distances (Å)

	Co120	Co120	Ni120	Ni120	Co170	Ni170
site	Co(1)	Co(2)	Ni(1)	Ni(2)		
M−OH$_2$	2.112(2)	2.086(2)	2.090(4)	2.036(4)	2.156(2)	2.163(2)
					2.008(2)	2.008(2)
M−OCO	2.067(2)	2.125(2)	2.049(4)	2.087(4)	2.160(2)	2.170(3)
					2.152(2)	2.168(2)
M−N	2.214(2)	2.185(2)	2.163(5)	2.113(5)	2.116(2)	2.204(3)
					2.183(2)	
						2.132(2)

Scheme 1. Two Possible Positions of *trans*-3(3-Pyridyl)acrylate



one temperature are isostructural. We will first describe the structure of the complexes prepared at 120 °C (**M120**) and then that at 170 °C (**M170**). The detail of the crystal data is given in Table 1.

Structure of M120. The structure of **M120** is shown in Figures 2 and 3, and the distances of the bonds around the metal centers are given in Table 2. The structure is composed of a 3D network of metal ions in octahedral coordination consisting of two water molecules, two unidentate carboxylates, and two pyridines in *trans* positions (Figure 2a). The ion sits on an inversion center, and thus, only three independent bond lengths are observed (Table 2). The two independent metal ions in the unit cell only differ in the orientation of the pyridine rings around the metal centers, represented by different dihedral angles between the plane of the aromatic ring and the plane defined by $H_2O-M(N)-H_2O$ (Figure 2b,c). We note that the metal−ligand distances are shorter for the nickel compound compared to that of cobalt as a result of the difference in ionic radii of the divalent metal ions (0.74 Å for Ni and 0.80 Å for Co). The network is generated by the connection of the pyridylacrylate ligand to other metal centers. Each metal center is coordinated to four independent pyridylacrylate units. Two of them are bonded via the nitrogen atoms of the pyridine and the other two via one of the oxygen atoms of the two carboxylate groups. The conformations of the ligands are also in pairs, two of each of those shown in Scheme 1. The rigidity of the C═C bond and the extended π-interactions limit the freedom of the carboxylate group and the rotation of the pyridine ring giving the two preferred orientations, while limited flexibility allows slightly different coordination geometries of the ligand. Thus, the limited rotational flexibility of the ligand allows a fairly closed packed 3D framework. The connections of the metals by the ligands generate three threads to form the close-packed structure. Importantly, the three threads are interwoven. However, the threads are independent of each other if the expansion of the lattice segment is limited to $2a \times 4b \times 2c$ (Figure 3a), and they merge at knots by covalent bonds if the lattice is expanded beyond these limits (Figure 3b) unlike the interpenetrated lattices reported in the literature, which are not covalently connected to one another.[31] Each thread can be visualized as a spiral staircase with a pitch of 4*b* connected to neighboring ones. Alternatively, the metal−$(H_2O)_2$ unit can be regarded as a tetrahedral node of a pseudodiamond network that interpenetrates within the unknotted limits.[31]

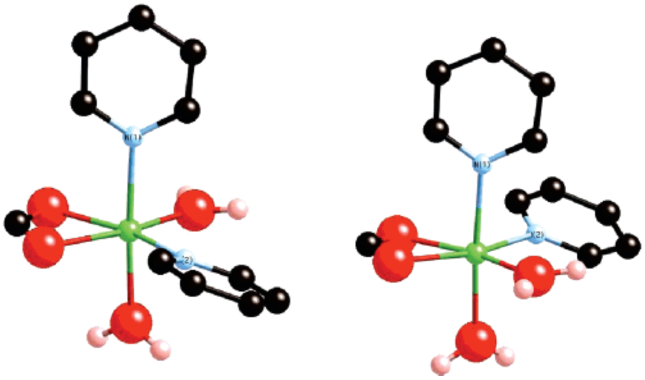


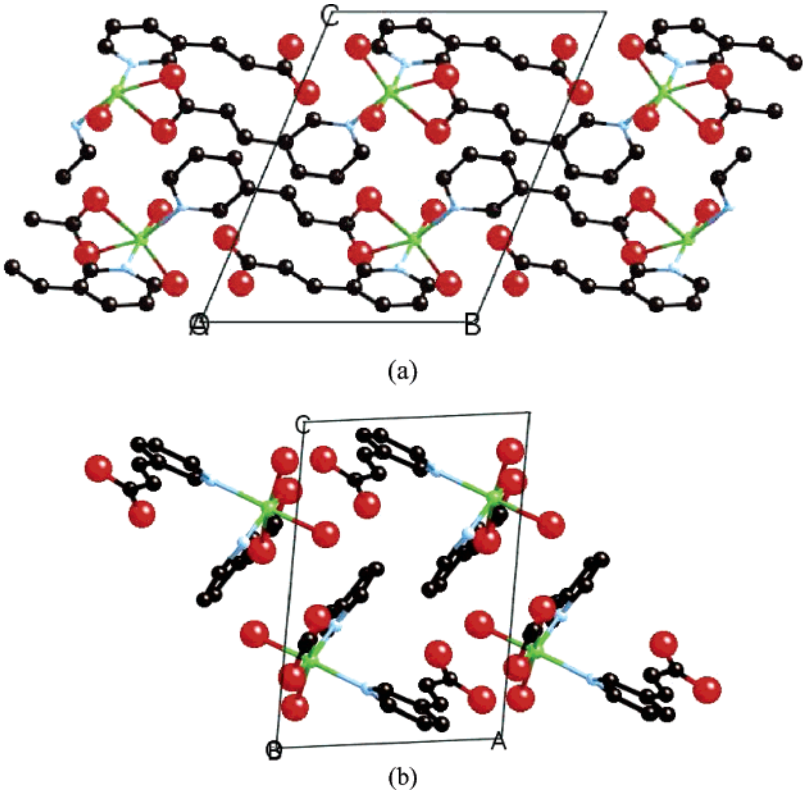
Figure 4. Coordination of the two symmetry related metal ions within the unit cell of the structure of **M170**. Note that the two entities are nonsuperposable.

Structure of M170. The compounds prepared at 170 °C are composed also of an octahedrally coordinated metal ion coordinated to two H_2O molecules, one bidentate carboxylate group, and two pyridines (Figure 4). In contrast to those prepared at 120 °C, the presence of the bidentate carboxylate group that automatically takes a *cis*-position leaves the water molecules and the pyridines to position either both in *cis* or one in *trans* and the other in *cis*; the former is observed in our case. It, therefore, has no center of symmetry, and all the six bonds are unique (Table 2). We note that the bond lengths are longer compared to those of the compounds prepared at 120 °C, and furthermore, the bond distances of the nickel compound (**Ni170**) are equal or slightly longer than those of the cobalt compound (**Co170**). We also note that the unit cell is larger for the nickel compared to the cobalt, contrary to expectations. Whether this is related to the Zwitterionic nature (see later) of the chain remains to be elucidated. The unit cell contains two octahedra that are related by the inversion center, and the two entities are not superimposable. These octahedra belong to two different chains running in opposite directions along the *b*-axis. The metal atoms are bridged into chains by only one of the two ligands via the pyridine nitrogen atom and the bidentate carboxylate group. The other ligand is terminal; it coordinates only via its nitrogen atom to the metal, and its carboxylate group is free (Figure 5). It is curious that the carboxylate group is free and still charged (−1) as required to balance the overall charge. There is no hydrogen bonding between the oxygen atoms and the surrounding hydrogen atoms. These compounds can be regarded as the inorganic equivalent of Zwitterions,[32] and furthermore, they are polymeric. Such a situation should produce an enhanced electric dipole that could favor nonlinear optical activity within one chain, but

---

(31) (a) Robson, R.; Batten, S. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247.

(32) Mercier, N.; Riou, A. *Chem. Commun.* **2004**, 844.



(a)

(b)

Figure 5. View of the structure of **M170** along the *a*-axis (a) and *b*-axis (b) showing the packing of chains and their opposite orientations, related by the inversion-center, along the *b*-axis. Hydrogen atoms are omitted for clarity.

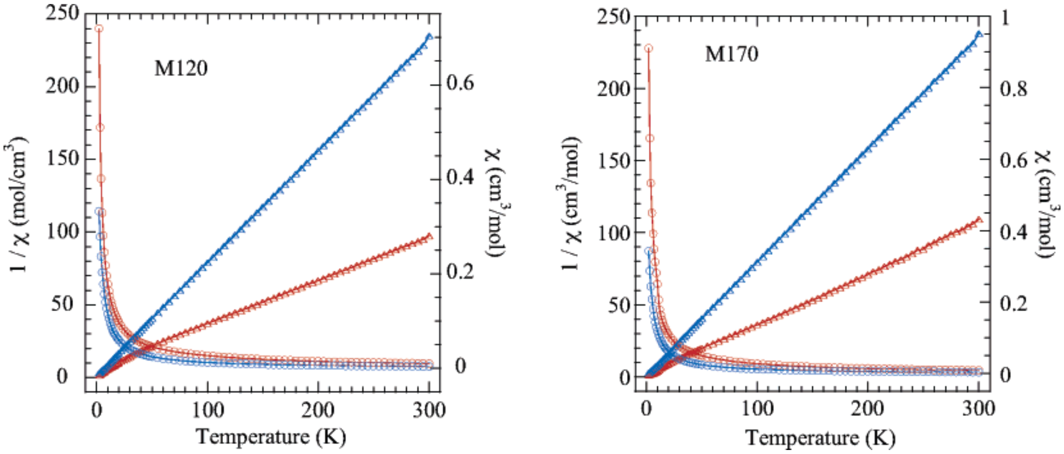


Figure 6. Temperature dependence of the susceptibility (○) and the inverse susceptibility (△) of the four compounds, nickel in blue and cobalt in red.

unfortunately in our case, this will be canceled by the opposite dipole of adjacent chains related by the inversion center.

As for the known compounds containing fused pyridinecarboxylate,[22,23] the present compounds formed with pyridylacrylate formed coordination polymers and also different polymorphs. However, compared to other isomers of pyridylacrylate,[25−27] the present compounds also display interpenetration of lattices but only on a small scale. As expected, the position of the pyridine (2-, 3-, or 4-) generates coordination polymers with different crystal structures.

Magnetic Properties. The magnetic properties were measured as a function of temperature in an applied field of 100 Oe and as a function of field at 2 K. Figure 6 shows the temperature dependence of the susceptibility and its inverse. The compounds behave in all cases as paramagnets with Curie constants {3.353(4) cm^{3}K/mol for **Co120**; 2.758(10) cm^{3}K/mol for **Co170**; 1.305(2) cm^{3}K/mol for **Ni120**; 1.279(2) cm^{3}K/mol for **Ni170**} close to that expected for the ions in octahedral coordination and with very weak exchange interactions as judged by the value of the Weiss constants {−24.1(3) K for **Co120**; +3(2) K for **Co170**; −2.9(3) K for **Ni120**; −2.1(3) K for **Ni170**}. The latter are in all three cases negative, suggesting weak antiferromagnetic interactions, and in one case (**Co170**), it is positive, suggesting ferromagnetic interaction between nearest neighbors. The isothermal magnetizations at 2 K (Figure 7) behave as expected with saturation values {2.21μ_B for **Co120**; 2.75μ_B for **Co170**;

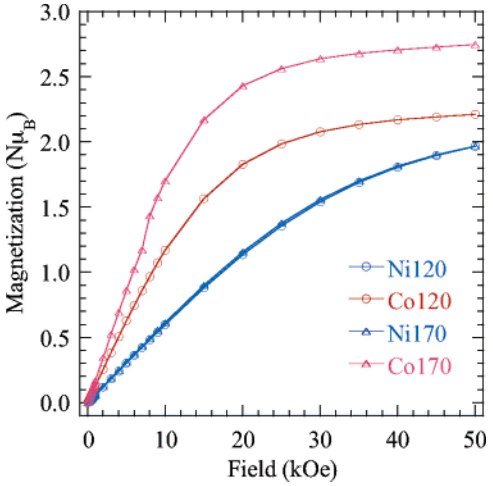


Figure 7. Isothermal magnetization of the four compounds at 2 K.

1.97μ_B for **Ni120**; 2.00μ_B for **Ni170**} within the range reported in the literature for paramagnetic nickel and cobalt complexes and is in agreement with an $S = 1$ for nickel and $S_{eff} = {}^1/_2$ for cobalt due to the important spin−orbit coupling resulting in only the $J = \pm{}^1/_2$ Kramers doublet being populated at 2 K.[33]

Conclusion. This work has evidenced an unusual crystallographic feature in coordination network of transition metals and *trans*-3(3-pyridyl)acrylate with the observation of interpenetrating lattices on a small scale merging into one on a higher scale. The second feature of interest is the polymorphism deriving from the conformation of the coordination at the metal site and its control at the synthetic stage by temperature. The third rare feature is the zwitterionic nature of coordination network. However, the long distance between the metal centers does not promote reasonable magnetic exchange interactions to provide long-range ordered magnets.

Acknowledgment. We thank the CNRS (France) and the Ministry of Education (Japan) for financing this work. H.K. thanks the JSPS (Japan) for a fellowship that allowed him to stay in Strasbourg. M.K. thanks the Royal Society of Chemistry for an author travel grant to visit IMS. We thank Prof. Zheming Wang (Peking University) for fruitful discussions concerning the structures.

Supporting Information Available: Crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org

IC0488536

---

[33] (a) Mabbs, F. E.; Machin, D. J. *Magnetism and transition metal complexes*; Chapman and Hall: London, 1973. (b) Herpin, A. *Theorie du Magnétisme*; Presse Universitaire de France: Paris, 1968.