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A tetrahedrally coordinated Ag^I and Ni^{II} complex with a two-dimensional framework containing one-dimensional helical chains

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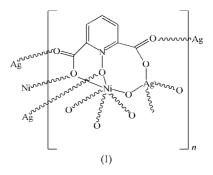
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The title complex, poly[bis(μ_6 -pyridine-2,6-dicarboxylato *N*-oxide)nickel(II)disilver(I)], $[Ag_2Ni(C_7H_3NO_5)_2]_n$ or $[Ag_2 Ni(pydco)_2]_n$ (H₂pydco = pyridine-2,6-dicarboxylic acid N-oxide), has a two-dimensional sheet structure. The two carboxylate groups adopt two coordination modes. The Ni^{II} ion displays a distorted octahedral geometry, bonded to two carboxylate O atoms of two different pydco ligands and four O donors from another two ligands, i.e. two carboxylate O atoms and two N-oxide O atoms. The Ag^I ion adopts a tetrahedral coordination, linked by three O atoms of three different carboxylate groups and an N-oxide O atom.

Comment

The design and synthesis of inorganic-organic composite coordination polymers exhibiting novel structures and properties have provided exciting new prospects (Cingolani et al., 2005; Dikarev et al., 2005). To date, a number of monometallic extended inorganic-organic composite materials have been synthesized by the combination of organic spacers and inorganic metal salts (Fujita et al., 1995). In contrast, mixed-metal organic-inorganic composite coordination polymers have not yet attracted much attention (Noro et al., 2005), although numerous bimetallic extended structures based on inorganic counter-ions such as cyanide have been reported (Larionova et al., 1999).

Pyridine-2,6-dicarboxylic acid N-oxide (H₂pydco) has limited steric hindrance and weak stacking interactions and can offer the possibility of forming coordination polymers either through one of its carboxylate groups, which is a versatile coordination mode in other organic aromatic polycarboxylate ligands, or through its N-oxide bridge, which is a far better electron donor than the ring N atom of pyridine-2,6-dicarboxylic acid (Nathan et al., 1985; Lin et al., 2006; Wen et al., 2005). Although its parent, pyridine-2,6-dicarboxylic acid, has been thoroughly studied, the coordination chemistry of H₂pydco has not been well explored hitherto. Therefore, much more work is required to extend our knowledge of the coordination behaviour of this ligand and its properties in forming coordination polymers. In contrast with the mixed metal-pydco system, to the best of our knowledge, no example of structural characterization has been reported. In this paper, we report the synthesis and crystal structure of the title compound, (I).



Compound (I) adopts a two-dimensional sheet structure with a one-dimensional helical chain. The Ni^{II} ion has a distorted octahedral geometry composed of two O atoms from carboxylate groups of two different pydco ligands and four O donors from another two pydco ligands, i.e. two carboxylate O atoms and two N-oxide O atoms. The Ag^I ion adopts a tetrahedral coordination, linked to three O atoms of three different carboxylate groups and N-oxide O atom (Fig. 1). The Ni-O bond lengths range from 1.917 (4) to 1.967 (4) Å, and the O-Ni-O bond angles range from 89.88 (8) to 180.0° .

The Ag^I centre adopts an AgO₄ coordination environment, which consists of three carboxylate O-atom donors from three different ligands and one O-atom donor from an N-oxide group of another pydco ligand (Fig. 2). All the Ag-O bond lengths are in good agreement with reported values (Dong et al., 2004), and the O-Ag-O bond angles range from 82.22 (7) to 135.0 (2)°.

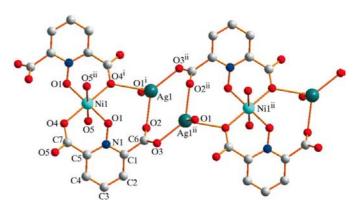


Figure 1

The molecular arrangement of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) 1 - x, 1 - y, 1-z; (ii) 2-x, 1-y, 2-z.]

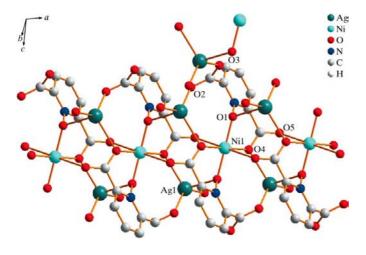


Figure 2

A partial packing view, showing the formation of the two-dimensionnal sheet. [Symmetry codes: (i) x - 1, y, z; (ii) 2 - x, 1 - y, 2 - z; (iii) 1 - x, 1 - y, 1 - z; (iv) 1 + x, y, z.]

The *N*-oxide groups exhibit a bridging coordination mode, while the carboxylate groups are coordinated to the Ag^I ions in an unprecedented bridging coordination mode, different from the monodentate mode observed in previous reports (Li et al., 2005). Thus, within the pydco ligand, the O atoms of the carboxylate groups exhibit two modes. One carboxylate group bridges one Ni^{II} ion and one Ag^I ion in a monodentate fashion involving only atom O4, while the other group adopts a bidentate mode via both O2 and O3, so each ligand links four Ag^I ions and two Ni^{II} ions. This results in a 16-membered metal-organic ring which is composed of two pydco ligands and two Ag^I ions, with one six-coordinated Ni^{II} ion located in the centre of the ring. These rings are linked through the pyridylcarboxylate groups to form one-dimensional zigzag chains (Fig. 2). Furthermore, the bridging O atoms of pydco extend adjacent chains by coordinating to the AgI and NiII atoms of the cyclic unit to generate a two-dimensional network (Fig. 2).

It noteworthy that, in this two-dimensional coordination polymer, there is one short ligand-supported Ag···Ag contact, Ag1···Ag1ⁱⁱ = 3.2859 (14) Å [symmetry code: (ii) 2 - x, 1 - y, 2 - z], which is less than the van der Waals diameter of Ag (3.44 Å).

In conclusion, this two-dimensional sheet structure with helical chains can be described as a new type of mixed-metal coordination polymer with the pydco ligand in which the framework is composed of tetrahedrally coordinated Ag^I and octahedrally coordinated Ni^{II} with the pydco ligand.

Experimental

A solution of $Na_2(pydco)$ (21.8 mg, 0.01 mmol) in CH_3CH_2OH (15 ml) was layered upon an aqueous solution of $NiCl_2 \cdot 2H_2O$ (16 mg, 0.016 mmol) and silver acetate (10 mg, 0.025 mmol). The resultant solution were kept at room temperature for three weeks and yielded pale-green crystals of (I).

Cr	vstal	data	

$\begin{bmatrix} Ag_2Ni(C_7H_3NO_5)_2 \end{bmatrix} \\ M_r = 636.66 \\ Triclinic, P\overline{1} \\ a = 4.9739 (9) \text{ Å} \\ b = 8.8459 (15) \text{ Å} \\ c = 9.1479 (16) \text{ Å} \\ \alpha = 93.829 (2)^{\circ} \\ \beta = 94.930 (2)^{\circ} \end{bmatrix}$	$\gamma = 103.0610 (10)^{\circ}$ $V = 389.09 (12) \text{ Å}^3$ Z = 1 Mo K α radiation $\mu = 3.76 \text{ mm}^{-1}$ T = 298 (2) K $0.25 \times 0.21 \times 0.18 \text{ mm}$
Data collection	
Bruker APEXII area-detector diffractometer Absorption correction: multi-scan (SADABS; Sheldrick, 1996) $T_{min} = 0.454, T_{max} = 0.551$ (expected range = 0.418–0.509)	2890 measured reflections 1422 independent reflections 1346 reflections with $I > 2\sigma(I)$ $R_{int} = 0.012$
Refinement	
$R[F^2 > 2\sigma(F^2)] = 0.045$ wR(F ²) = 0.097 S = 1.14	133 parameters H-atom parameters constrained $\Delta \rho_{\text{max}} = 3.04 \text{ e} \text{ Å}_{\circ}^{-3}$

The H atoms were positioned geometrically and treated as riding on their parent atoms, with C-H distances of 0.93 Å, and with $U_{iso}(H) = 1.2U_{ea}(C)$.

 $\Delta \rho_{\rm min} = -2.51 \text{ e} \text{ Å}^{-3}$

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3061). Services for accessing these data are described at the back of the journal.

References

1422 reflections

- Bruker (1998). SHELXTL. Version 5.1. Bruker AXS Inc, Madison, Wisconsin, USA.
- Bruker (1999). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2004). APEX2. Version 1.22. Bruker AXS Inc, Madison, Wisconsin, USA.
- Cingolani, A., Galli, S., Masciocchi, N., Pandolfo, L., Pettinari, C. & Sironi, A. (2005). J. Am. Chem. Soc. 127, 6144–6145.
- Dikarev, E. V., Zhang, H. & Li, B.-J. (2005). J. Am. Chem. Soc. 127, 6156–6157.
 Dong, Y.-B., Zhao, X., Huang, R.-Q., Smith, M. D. & Zur Loye, H.-C. (2004).
 Inorg. Chem. 43, 5603–5612.
- Fujita, M., Kwon, Y. J., Sasaki, O., Yamaguchi, K. & Ogura, K. (1995). J. Am. Chem. Soc. 127, 7287–7288.
- Larionova, J., Kahn, O., Gohlen, S., Ouahab, L. & Clérac, R. (1999). J. Am. Chem. Soc. 121, 3349–3350.
- Li, F.-F., Ma, J.-F., Song, S.-Y., Yang, J., Liu, Y.-Y. & Su, Z.-M. (2005). Inorg. Chem. 44, 9374–9383.
- Lin, J.-G., Zhu, H.-Z., Wen, L.-L., Tian, Z.-F. & Meng, Q.-J. Z. (2006). Z. Anorg. Allg. Chem. 632, 689–694.
- Nathan, L. C., Doyle, C. A., Mooring, A. M., Zapien, D. C., Larsen, S. K. & Pierpont, C. G. (1985). *Inorg. Chem.* 24, 2763–2766.
- Noro, S.-I., Miyasaka, H., Kitagawa, S., Wada, T., Okubo, T., Yamashita, M. & Mitani, T. (2005). *Inorg. Chem.* 44, 133–146.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Wen, L.-L., Dang, D.-B., Duan, C.-Y., Li, Y.-Z., Tian, Z.-F. & Meng, Q.-J. (2005). Inorg. Chem. 44, 7161–7170.