

Ni(bipy)₂Ni(CN)₄, a new type of one-dimensional square tetracyano complex

Juraj Černák^{a*} and Khalil A. Abboud^b

^aDepartment of Inorganic Chemistry, P. J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia, and ^bDepartment of Chemistry, University of Florida, PO Box 117200, Gainesville, Florida 32611-7200, USA
Correspondence e-mail: cernakju@kosice.upjs.sk

Received 10 December 1999

Accepted 2 April 2000

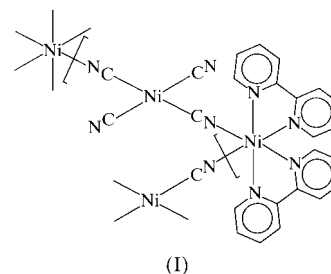
The one-dimensional structure of *catena*-poly[[bis(2,2′-bipyridyl-1κ²N,N′)-μ-cyano-1:2κ²N:C-dicyano-2κ²C-dinickel(II)]-μ-cyano-C:N], [Ni₂(CN)₄(C₁₀H₈N₂)₂]_n, consists of infinite zigzag chains running parallel to the *c* axis. The chains are composed of paramagnetic [Ni(bipy)₂]²⁺ cations (bricks; nickel on a twofold axis) linked by diamagnetic [Ni(CN)₄]²⁻ anions (mortar; nickel on an inversion center) *via* bridging cyano groups. The bridging cyano groups occupy *cis* positions in the cation and *trans* positions in the anion, giving rise to a new previously unknown CT-type chain (*i.e.* *cis-trans*-type) among square tetracyano complexes. The coordination polyhedron of the paramagnetic Ni atom (twofold symmetry) is a slightly deformed octahedron with the two Ni–N(bipy) bonds in *cis* positions being somewhat longer [2.112 (3) Å] than the remaining four Ni–N bonds with a mean value of 2.065 (6) Å. The bond distances and angles in the anion have typical values.

Comment

One-dimensional magnetic materials are of current interest due to their interesting magnetic properties (Dagotto, 1996; Chen & Suslick, 1993; Orendáč *et al.*, 1995; Delhaes & Drillon, 1987). The synthetic strategy of such materials can be based on the use of the so-called ‘brick and mortar’ method (Willett *et al.*, 1993), where paramagnetic entities (bricks) are linked by suitable bridging units (mortar). Square-planar tetracyano complexes are suitable bridging units due to the possibility of using cyano groups to link metal atoms. Stereochemical considerations and literature data (Iwamoto, 1996) indicate that various types of one-dimensional structures may be formed. As examples of different types of one-dimensional structures, we can mention Ni(en)₂Ni(CN)₄ exhibiting a TT-type chain structure [two bridging cyano groups occupy *trans* (T) positions in both the cation and anion; Černák, Chomič *et al.*, 1988], diamagnetic Cd(en)₂Ni(CN)₄ (two polymorphs, en is ethylenediamine) forming CC-type chains (Yuge *et al.*, 1995),

Ni(en)₂Ni(CN)₄·*n*H₂O with more complicated CCTC-type chains (periodicity doubled; Černák *et al.*, 1990) and [Eu(dmf)₄Ni(CN)₄] (dmf is dimethylformamide) exhibiting a ladder-like one-dimensional structure with three bridging cyano groups (Knoeppel & Shore, 1996). To date, no crystal structures with CT- or TC-type chains containing square-planar tetracyano complexes as bridging units have been reported.

The results of crystal structure analyses of the one-dimensional compounds [Ni(bipy)₂N₃]ClO₄ and [Ni(bipy)₂N₃]PF₆ (Urriaga *et al.*, 1994) have shown that the presence of two bulky 2,2′-bipyridine (bipy) ligands in the nickel octahedral coordination sphere leads to zigzag-type chains. CT-type chains were found in [Cu(bipy)₂Ag₂(CN)₄]·H₂O, a compound with linear dicyanoargentate anions (Černák *et al.*, 1993). These results indicate that the Ni(bipy)₂Ni(CN)₄ compound, (I), initially described a long time ago (Feigl *et al.*, 1945), may be a good candidate for a CT (or CC) type chain. The results of its crystal structure analysis are reported here and are discussed with respect to similar one-dimensional structures containing square-planar tetracyano complex anions.



The centrosymmetric structure of the title compound consists of zigzag-type chains. The chains are composed of paramagnetic [Ni(bipy)₂]²⁺ cations (bricks), which are linked by diamagnetic [Ni(CN)₄]²⁻ anions (mortar). The bridging cyano groups occupy *cis* positions in the cation, thereby completing the chromophore to NiN₄N₂. On the other hand, they occupy *trans* positions in the anion, giving rise to a CT-type chain not yet found among square tetracyano complexes. Only van der Waals forces operate between the chains, so the packing of the chains is directed mainly by geometric requirements. The shortest distance between two atoms of neighboring chains is 2.42 (1) Å [H11A...H4A(*x* – ½, *y* – ½, ½ – *z*)], which is in line with the sum of the van der Waals radii of H atoms (2.40 Å; Taylor & Kennard, 1982). The shortest distance between two paramagnetic Ni atoms is 8.681 (1) Å [*e.g.* Ni2...Ni2(*x* – ½, *y* – ½, ½ – *z*)], but there is no effective bridging between these atoms. Two paramagnetic Ni atoms (Ni2) within the chain are separated by 10.116 (2) Å and the –N–C–Ni–C–N– five-atom bridge may serve as an exchange path for the observed superexchange-type interaction (Orendáč *et al.*, 2000). The bridge is quite linear; the greatest deviation from linearity is represented by the Ni2–N2–C2–(Ni1) angle [171.1 (3)°]. Similar but positively charged chains were found in the [Cu(bipy)₂Ag₂(CN)₄]·H₂O compound with linear dicyanoargentate anions, where the positive charge of the chains is counterbalanced by the

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.142$
 $S = 1.007$
 2591 reflections
 156 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 1.2512P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.19 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ni1—C1	1.860 (6)	Ni2—N3	2.060 (4)
Ni1—C2	1.871 (4)	Ni2—N4	2.112 (3)
Ni2—N2	2.070 (3)		
C1 ⁱ —Ni1—C1	180.0	N3 ⁱⁱ —Ni2—N2 ⁱⁱ	91.3 (1)
C1 ⁱ —Ni1—C2	92.6 (2)	N2 ⁱⁱ —Ni2—N2	92.7 (2)
C1—Ni1—C2	87.4 (2)	N3—Ni2—N4	79.0 (1)
C2—Ni1—C2 ⁱ	180.0 (2)	N3 ⁱⁱ —Ni2—N4	93.3 (1)
N3—Ni2—N3 ⁱⁱ	169.5 (2)	N2 ⁱⁱ —Ni2—N4	174.2 (1)
N3—Ni2—N2 ⁱⁱ	96.0 (1)	N2—Ni2—N4	90.3 (1)

Symmetry codes: (i) $-x, 2 - y, -z$; (ii) $-x, y, \frac{1}{2} - z$.

The H atoms were placed in idealized positions and were refined riding on their parent atoms. A C—H distance of 0.95 Å was used for all Csp^2 atoms. The H-atom displacement parameters were set at $1.2U_{eq}$ of the parent C atom. Full data collection details are reported elsewhere (Abboud *et al.*, 1997). Four data sets using four different crystals were collected for this structure and each solution revealed the presence of disorder in the position of the two bipyridine ligands. The data reported here have the least disorder (less than 5%) and it was not possible to resolve.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1998) and *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported, in part, by the National Science Foundation (NSF INT-9722935). Partial support from the grant agency VEGA (No. 1/7426/20) is also acknowledged. KAA wishes to acknowledge the National Science Foundation

and the University of Florida for funding the purchase of the X-ray equipment. We have benefited from interactions with M. W. Meisel, who reviewed the manuscript.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1357). Services for accessing these data are described at the back of the journal.

References

- Abboud, K. A., Ortiz, C. G., Palenik, R. C. & Palenik, G. J. (1997). *Acta Cryst.* **C53**, 1322–1323.
- Akyüz, S., Ozel, A. E., Davies, J. E. & Bakiler, M. (1996). *J. Incl. Phenom. Mol. Recognit. Chem.* **26**, 103–109.
- Bruker (1998). *SMART, SAINT and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Černák, J., Chomič, J., Baloghová, D. & Dunaj-Jurčo, M. (1988). *Acta Cryst.* **C44**, 1902–1905.
- Černák, J., Chomič, J., Domiano, P., Ori, O. & Andreetti, G. D. (1990). *Acta Cryst.* **C46**, 2103–2107.
- Černák, J., Dunaj-Jurčo, M., Melník, M., Chomič, J. & Skoršepa, J. (1988). *Rev. Inorg. Chem.* **9**, 259–281.
- Černák, J., Gérard, F. & Chomič, J. (1993). *Acta Cryst.* **C49**, 1294–1296.
- Černák, J., Lengyelová, E., Ahmadi, K. & Hardy, A.-M. (1996). *J. Coord. Chem.* **37**, 55–62.
- Chen, C. T. & Suslick, K. S. (1993). *Coord. Chem. Rev.* **128**, 292–322.
- Dagotto, E. (1996). *Phys. World*, April, p. 22.
- Delhaes, P. & Drillon, M. (1987). Editors. *Organic and Inorganic Low-Dimensional Crystalline Materials*. New York: Plenum Press.
- Feigl, F., Demant, V. & de Oliveira, E. (1945). *An. Assoc. Quim. Bras.* **3**, 72–87; *Chem. Abstr.* **39**, 3219.
- Iwamoto, T. (1996). *J. Incl. Phenom.* **24**, 61–132.
- Kepert, D. L. (1982). In *Inorganic Stereochemistry*. Berlin: Springer-Verlag.
- Knoepfel, G. W. & Shore, S. G. (1996). *Inorg. Chem.* **35**, 5328–5334.
- Orendáč, M., Čizmár, E., Orendáčová, A., Černák, J., Feher, A., Meisel, M., Abboud, K. A., Zvyagin, S., Sieling, M. & Lüthi, M. (2000). *Phys. Rev. B*, **61**, 3223–3226.
- Orendáč, M., Orendáčová, A., Černák, J., Feher, A., Signore, P. J. C., Meisel, M. W. & Verdager, M. (1995). *Phys. Rev. B*, **52**, 3435–3440.
- Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
- Urriaga, M. K., Arriortua, M. I., De Muro, I. G. & Cortes, R. (1995). *Acta Cryst.* **C51**, 62–65.
- Urriaga, M. K., Pizarro, J. L., Goñi, A., Lezama, L. & Cortes, R. (1994). Book of Abstracts of the 15th ECM, Dresden, Germany, p. 696. Oldenbourg Verlag.
- Wada, A., Sakabe, N. & Tanaka, J. (1976). *Acta Cryst.* **B32**, 1121–1127.
- Willett, R. G., Wang, Z., Molnar, S., Brewer, K., Landee, C. P., Turnbull, M. M. & Zhang, W. (1993). *Mol. Cryst. Liq. Cryst.* **233**, 277–282, and references therein.
- Yuge, H., Mamada, A., Asai, M., Nishikiori, S. & Iwamoto, T. (1995). *J. Chem. Soc. Dalton Trans.* pp. 3195–3205.