Crystallochemistry of tetracyano complexes
Crystal and molecular structure of bis[tetraamminecopper(II)-μ-cyano-dicyanonickelate(II)-μ-cyano-*cyclo*-(bisdiamminecopper(II)-di-μ-cyano-dicyanonickelate(II))]

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Dedicated to Professor P. Kristian, DrSc., in honour of his 60th birthday

$C_{16}H_{36}N_{28}Cu_4Ni_4$, $M_r = 1109.64$, orthorhombic, Pnnm, $a = 1577.2(5)$ pm, $b = 1683.8(4)$ pm, $c = 733.3(1)$ pm, $V = 1.9474(8) \times 10^9$ pm^3, $Z = 2$, $D_m = 1.91(1)$, $D_c = 1.89$ Mg m^{-3}, μ(Cu$K\alpha$) = 4810 m^{-1}, $F(000) = 1112e^-$, $T = 293$ K, $R = 0.0615$, 771 observed reflections. The unit cell contains two planar centrosymmetric octanuclear molecules. These are built up of a cycle and two terminal groups. The cycle consists of two *cis*-$[Ni(CN)_2$-μ-$(CN)_2]^{2-}$ anions bridged by two $[Cu(NH_3)_2]^{2+}$ cations. Two terminal groups with the composition $[(NH_3)_4Cu$-μ-$(NC)Ni(CN)_2$-μ-(CN)—] are bonded to the Cu atoms in the cycle. The coordination geometry of the Ni atoms is square-planar. The coordination polyhedrons of the copper atoms are very distorted trigonal bipyramids (in the cycle) and tetragonal pyramids (in the terminal groups). Two angles of the type —C≡N—Cu exhibit unusual low values 126(1)° and 141(1)°.

$C_{16}H_{36}N_{28}Cu_4Ni_4$, $M_r = 1109{,}64$, орторомбическая, Pnnm, $a = 1577{,}2(5)$ пм, $b = 1683{,}8(4)$ пм, $c = 733{,}3(1)$ пм, $V = 1{,}9474(8) \cdot 10^9$ пм^3, $Z = 2$, $D_m = 1{,}91(1)$, $D_c = 1{,}89$ Мг м$^{-3}$, μ(Cu$K\alpha$) = 4810 м$^{-1}$, $F(000) = 1112e^-$, $T = 293$ K, $R = 0{,}0615$, 771 наблюдаемых отражений. Элементарная ячейка содержит две плоские центросимметричные восьмиядерные молекулы. Они построены из цикла и двух конечных групп. Цикл состоит из двух *цис*-$[Ni(CN)_2$-μ-$(CN)_2]^{2-}$ анионов, соединенных мостиком из двух катионов $[Cu(NH_3)_2]^{2+}$. Две конечные группы состава $[(NH_3)_4Cu$-μ-$(NC)Ni(CN)_2$-μ-(CN)—] связаны с атомами Cu в цикле. Координационная геометрия атомов Ni квадратно-плоская. Координационные многогранники атомов меди представляют собой сильно искаженную тригональную бипирамиду (в цикле) и тетрагональные пирамиды (в конечных группах). Два угла типа —C≡N—Cu имеют необычно низкие величины 126(1)° и 141(1)°.

Tetracyanonickelates(II) form different structure types. We have determined the structure of a series of complexes crystallizing from the systems: M^{2+}—NH_3—$[Ni(CN)_4]^{2-}$—H_2O and M^{2+}-en-$[Ni(CN)_4]^{2-}$—H_2O (M = Cu, Ni, Zn, Cd) to explain their thermal and other properties. Complexes represented by the formula $M^{2+}(NH_3)_3Ni(CN)_4$ (M = Cu, Zn, Cd) were prepared from the NH_3 system [1]. We report on the crystal structure of the copper complex (M = Cu).

Experimental

Blue needle shape crystal with a maximum dimension 0.6 mm of the title complex was obtained as described elsewhere [1], D_m by flotation in a mixture of $CHBr_3$ and CH_3COCH_3. Preliminary Weissenberg photographs indicated the possible space groups as Pnnm or Pnn2. The centrosymmetric choice was confirmed by the structure analysis. Data collection: Syntex $P2_1$ diffractometer, graphite monochromatized Cu$K\alpha$ radiation, unit cell parameters from 13 reflections with $6.65° \leq \Theta \leq 15.80°$. Θ—2Θ scan technique, scan angle from $(2\Theta(\mathrm{Cu}K\alpha_1) - 1)°$ to $(2\Theta(\mathrm{Cu}K\alpha_2) + 1)°$. 1105 unique reflections ($0 \leq h \leq 16$, $0 \leq k \leq 17$, $0 \leq l \leq 8$) with $0 \leq 2\Theta \leq 98.5°$, of these 771 had $F_0 \geq 4\sigma(F_0)$. Standard reflections 221 and 202 were used for orientation and intensity control every 98 reflections, intensities were corrected for the variation (± 5 % of mean values) observed with the standard reflections along L_p corrections using the XP21 program [2]. Absorption corrections were performed using the program ABSORB [3], the maximum and minimal values of the transmission factors were 1.214 and 0.853. The structure was solved using the program SHELXS '86 [4]. Full matrix least-squares refinement was applied using the program SHELX '76 [5]. $\Sigma w(\Delta F)^2$ was minimized using a weighting scheme $w = (\sigma^2(F_0) + 0.002\,F_0^2)^{-1}$ which showed no systematic shiftings as a function of F_0. Final $R = 0.0615$, $wR = 0.0780$, $S = 1.37$ (148 parameters varied), $(\Delta/\sigma)_{max} = 0.03$. The last difference map showed four maxima in the range 0.91—1.21 e Å^{-3} near the four heavy atoms, elsewhere $-0.48 \leq \Delta\varrho \leq 0.73$ e Å^{-3}. Scattering factors were taken from [6] (Cu, Ni) and SHELX '76 [5]. Molecules of NH_3 (labelled A(i)) were approximated assuming free rotation model, which is a better approximation to an ammonia molecule (whether rotating or not) than an isolated nitrogen atom [7]. Calculations were performed on EC 1045 computer in the Computer Centre of the Technical University of Košice. Geometrical analysis was performed using PARST [8]. Tables of the observed and calculated values of the structure factors can be obtained on request from the authors.

Discussion

Final atomic positional parameters are given in Table 1. Anisotropic thermal parameters are given in Table 2. The structure consists of centrosymmetric planar octanuclear molecules (Fig. 1). These are built up of a cycle and two terminal groups. The cycle is built up of two *cis*-$[\mu\text{-}(NC)_2Ni(CN)_2]^{2-}$ (Ni(1)

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($10^{-20}\,m^2$) with e.s.d.'s in the parentheses $\left(B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j a_i^* a_j^* \bar{a}_i \bar{a}_j\right)$

Atom	x/a	y/b	z/c	B_{eq}
Cu(1)	5447(2)	1394(1)	0	3.22(7)
Cu(2)	6080(2)	6265(1)	0	3.53(8)
Ni(1)	2588(2)	960(2)	0	3.33(8)
Ni(2)	7604(2)	3665(2)	0	3.17(8)
A(1)	5370(6)	1352(5)	2716(13)	3.5(3)
A(2)	7005(7)	6380(6)	1958(13)	4.4(3)
A(3)	5200(6)	6271(5)	2001(14)	4.2(3)
N(11)	4196(10)	1919(10)	0	4.0(5)
N(12)	3773(11)	−475(11)	0	4.5(5)
N(13)	1122(12)	−161(11)	0	5.1(6)
N(14)	1516(12)	2424(10)	0	4.9(6)
N(21)	6290(11)	2408(9)	0	3.5(5)
N(22)	6236(11)	4901(10)	0	4.3(5)
N(23)	8833(13)	5031(13)	0	6.3(6)
N(24)	9011(10)	2462(9)	0	3.9(5)
C(11)	3578(12)	1583(11)	0	3.2(5)
C(12)	3323(12)	68(13)	0	3.7(6)
C(13)	1655(13)	304(12)	0	3.5(6)
C(14)	1883(13)	1861(11)	0	3.6(5)
C(21)	6825(12)	2870(10)	0	2.6(5)
C(22)	6731(13)	4444(12)	0	3.4(6)
C(23)	8367(12)	4498(12)	0	3.8(6)
C(24)	8469(12)	2925(10)	0	2.9(6)

atom) anions and two $[Cu(NH_3)_2]^{2+}$ cations (Cu(1) atom). The terminal groups are placed symmetrically through the centre of symmetry and are built up of *cis*-$[\mu\text{-(NC)Ni(CN)}_2\text{-}\mu\text{-(CN)}]^{2-}$ (Ni(2) atom) and $[Cu(NH_3)_4]^{2+}$ (Cu(2) atom) ions. The terminal groups are attached to the Cu(1) atoms through the μ-cyano groups. This is the novel structure type, not yet described among the tetracyanonickelate(II) complexes.

The coordination geometry of Ni(1) and Ni(2) atoms is square-planar with two μ-cyano groups in *cis* positions. The *cis* arrangement of the μ-cyano groups was observed only in $Ni(en)_2Ni(CN)_4 \cdot 2.5H_2O$ complex, usually a *trans* arrangement was observed in $[Ni(CN)_4]^{2-}$ anions [9]. The bond distances and angles (Table 3) in $[Ni(CN)_4]^{2-}$ are not significantly different from the expected values [10].

Table 2

Coefficients of anisotropic temperature factors ($\times 10^2$) with e.s.d.'s in the parentheses. The temperature factor is in the form $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{12}a^*b^*hk)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	3.7(2)	3.9(2)	4.6(2)	0	0	−0.0(1)
Cu(2)	4.2(2)	3.6(2)	4.7(2)	0	0	0.2(1)
Ni(1)	4.1(2)	4.1(2)	4.4(2)	0	0	0.3(2)
Ni(2)	3.9(2)	3.3(2)	4.8(2)	0	0	−0.6(2)
A(1)	5.5(6)	4.6(5)	3.4(6)	0.4(5)	0.6(5)	0.4(5)
A(2)	6.6(7)	6.1(7)	4.1(7)	−0.2(6)	−0.7(6)	−0.9(6)
A(3)	5.1(7)	5.7(6)	5.1(7)	−0.3(6)	0.3(6)	−0.2(5)
N(11)	4.4(11)	6.6(11)	4.3(11)	0	0	−0.6(10)
N(12)	5.0(11)	8.4(14)	3.5(10)	0	0	1.2(11)
N(13)	6.6(13)	6.2(12)	6.4(12)	0	0	−0.4(11)
N(14)	7.0(15)	5.4(13)	6.2(12)	0	0	0.9(11)
N(21)	4.2(10)	4.7(10)	4.3(10)	0	0	−0.8(9)
N(22)	5.9(12)	5.6(11)	4.9(11)	0	0	0.8(11)
N(23)	8.3(15)	8.8(14)	6.8(13)	0	0	−3.1(13)
N(24)	4.7(12)	4.9(11)	4.9(11)	0	0	0.2(9)
C(11)	3.0(12)	4.4(12)	4.6(12)	0	0	1.0(10)
C(12)	2.5(11)	7.2(15)	4.3(13)	0	0	0.2(12)
C(13)	3.7(12)	4.7(13)	4.7(13)	0	0	1.2(10)
C(14)	6.1(14)	3.2(12)	4.6(12)	0	0	1.2(12)
C(21)	3.1(12)	3.4(11)	3.5(11)	0	0	0.7(10)
C(22)	3.4(12)	4.8(13)	4.5(12)	0	0	−0.3(11)
C(23)	4.5(13)	6.9(15)	3.2(12)	0	0	0.9(12)
C(24)	4.0(12)	3.6(12)	3.5(12)	0	0	−0.7(10)

Although both Cu(1) and Cu(2) atoms have the same coordination number 5, they are different from crystallochemical and geometrical point of view. Nevertheless, this is the first example of a tetracyanonickelate structure where the central atom of the complex cation has a coordination number different from six [11].

The coordination geometry of the Cu(1) atom could be described as a very distorted trigonal bipyramid with two NH_3 molecules (A(1)) in the axial positions and three *N*-bonded μ-cyano groups in the equatorial plane, or a very deformed square pyramid. This deformed coordination geometry is probably a consequence of the fact that the Cu(1) atom lies in the cycle. On the other hand, the Cu(2) atom exhibits square-pyramidal coordination with the *N*-bonded μ-cyano group in the apical position. The corners of the basal plane are occupied

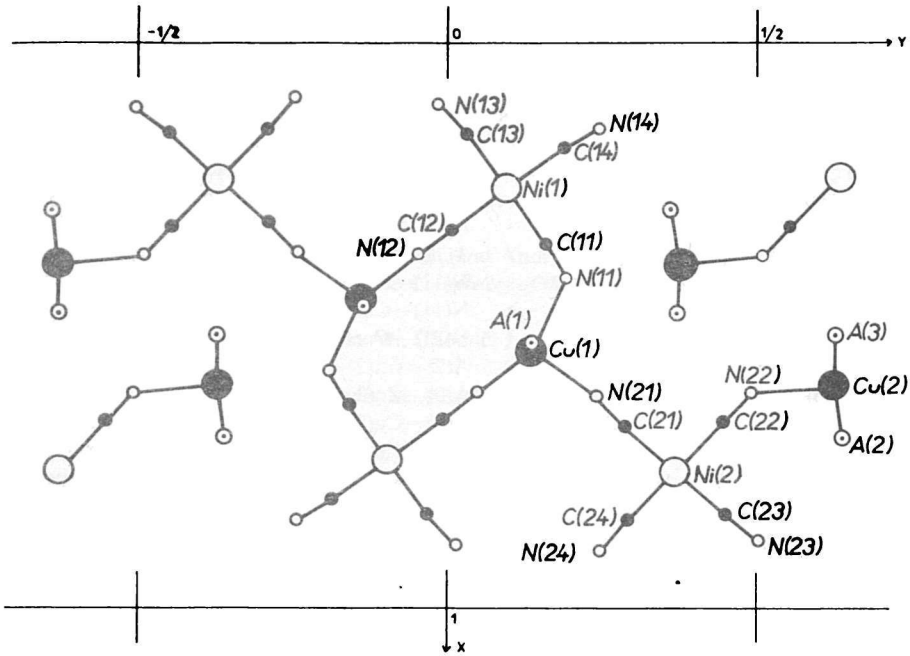

Fig. 1. View of the structure of $[Cu(NH_3)_3Ni(CN)_4]$ down the z axis.

by NH_3 molecules (A(2) and A(3)). The Cu(2) atom is displaced 9.9(2) pm from the basal plane to the apex of the pyramid. The Cu—N(NH_3) bond distances are within 202—206(1) pm. On the other hand, the Cu—N(N≡C) bonds differ significantly from 198(2) pm to 231(2) pm, but these values are in the range found for Cu—N bonds in other Cu(II) complexes [12].

Two C≡N—Cu angles (Table 3) exhibit low values (126(1)° and 141(1)°) compared with the usually observed values 150—180°. A similar low value (123.1(5)°) was observed in the $Cu(en)_2Ni(CN)_4$ complex [13].

The octanuclear molecules are held together by weak hydrogen bonds of the N—H···N(≡C) type; the A(1)···N(23)' distance being 306(2) pm (' $1.5 - x$, $0.5 - y$, 0.5), the A(1)···N(14)'' distance being 321(2) pm (" $0.5 - x$, $0.5 - y$, 0.5) and A(3)···N(13)''' distance being 323(2) pm (''' $0.5 + x$, $0.5 - y$, $0.5 \pm z$). The other contacts are > 323 pm. The only exception is the contact Cu(2)···N(11)^{IV} ($^{IV}1 - x$, $1 - y$, z) 309(2) pm. On the basis of MO quantum-chemical calculations it was pointed out that in the $Cu(NH_3)_4Cu_4(CN)_6$ complex there exists a weak π-bonding interaction between the Cu^{2+} atom and the triple

Table 3

Bond distances (pm) and angles (°) with e.s.d.'s in the parentheses

Atoms	Distances	Atoms	Angles
Cu(1)—A(1)	200(1)	A(1)—Cu(1)—A(1)"	171.9(4)
Cu(1)—N(11)	216(2)	A(1)—Cu(1)—N(11)	87.7(3)
Cu(1)—N(12)'	198(2)	A(1)—Cu(1)—N(12)'	90.6(3)
Cu(1)—N(21)	216(2)	A(1)—Cu(1)—N(21)	93.8(3)
		N(11)—Cu(1)—N(12)'	152.6(6)
		N(11)—Cu(1)—N(21)	103.8(5)
		N(21)—Cu(1)—N(12)'	103.6(6)
Cu(2)—A(2)	206(1)	A(2)—Cu(2)—A(3)	88.8(4)
Cu(2)—A(3)	202(1)	A(2)—Cu(2)—A(2)"	88.6(4)
Cu(2)—N(22)	231(2)	A(3)—Cu(2)—A(3)"	93.2(4)
		A(2)—Cu(2)—N(22)	91.0(3)
		A(3)—Cu(2)—N(22)	94.5(2)
Ni(1)—C(11)	188(2)	C(11)—Ni(1)—C(12)	86.2(7)
Ni(1)—C(12)	190(2)	C(11)—Ni(1)—C(14)	92.3(7)
Ni(1)—C(13)	184(2)	C(12)—Ni(1)—C(13)	90.8(7)
Ni(1)—C(14)	188(2)	C(13)—Ni(1)—C(14)	90.7(7)
Ni(2)—C(21)	182(2)	C(21)—Ni(2)—C(22)	91.1(7)
Ni(2)—C(22)	190(2)	C(21)—Ni(2)—C(24)	90.1(7)
Ni(2)—C(23)	185(2)	C(22)—Ni(2)—C(23)	87.0(7)
Ni(2)—C(24)	185(2)	C(23)—Ni(2)—C(24)	91.8(7)
N(11)—C(11)	113(2)	Ni(1)—C(11)—N(11)	176(1)
N(12)—C(12)	116(3)	Ni(1)—C(12)—N(12)	180(2)
N(13)—C(13)	115(3)	Ni(1)—C(13)—N(13)	174(2)
N(14)—C(14)	111(3)	Ni(1)—C(14)—N(14)	175(2)
N(21)—C(21)	115(2)	Ni(2)—C(21)—N(21)	175(1)
N(22)—C(22)	110(3)	Ni(2)—C(22)—N(22)	179(2)
N(23)—C(23)	116(3)	Ni(2)—C(23)—N(23)	179(2)
N(24)—C(24)	116(2)	Ni(2)—C(24)—N(24)	180(1)
		Cu(1)—N(11)—C(11)	126(1)
		Cu(1)—N(12)'—C(12)'	179(1)
		Cu(2)—N(22)—C(22)	141(1)

Symmetry codes: '$1-x, -y, -z$; "$x, y, -z$.

bond of the cyano group for a distance 297(1) pm [14] which is by 12 pm shorter than in the $Cu(NH_3)_3Ni(CN)_4$ complex.

References

1. Černák, J. and Chomič, J., *J. Therm. Anal.* *32*, 527 (1987).
2. Pavelčík, F., *Program XP21*. Faculty of Pharmacy, Comenius University, Bratislava, 1986.

3. Ugozzoli, F., *Comput. Chem. 11*, 109 (1987).
4. Sheldrick, G. M., *SHELXS '86*. Program for Solution of Crystal Structures. University of Göttingen, GFR, 1986.
5. Sheldrick, G. M., *SHELX '76*. Program for Crystal Structure Determination. University of Cambridge, England, 1976.
6. *International Tables for X-Ray Crystallography*, Vol. *IV*. Kynoch Press, Birmingham, 1974.
7. Williams, R. J., Cromer, D. T., and Larson, A. C., *Acta Crystallogr., B27*, 1701 (1971).
8. Nardelli, M., *Comput. Chem. 7*, 95 (1983).
9. Černák, J., Chomič, J., Domiano, P., Ori, O., and Andreetti, G. D., unpublished results.
10. Sharpe, A. G., *The Chemistry of the Cyano Complexes of the Transition Metals*. Academic Press, London, 1976.
11. Černák, J., Dunaj-Jurčo, M., Melník, M., Chomič, J., and Skoršepa, J., *Rev. Inorg. Chem. 9*, 259 (1988).
12. Gažo, J., Boča, R., Jóna, E., Kabešová, M., Macášková, L., Šima, J., Pelikán, C., and Valach, F., *Coord. Chem. Rev. 43*, 87 (1982).
13. Dunaj-Jurčo, M., Garaj, J., Chomič, J., Haluška, V., and Valach, F., *Proceedings of the 6th Conference on Coordination Chemistry*, p. 45. Bratislava—Smolenice, 1976; *Chem. Abstr. 90*, 64844 U.
14. Dunaj-Jurčo, M. and Boča, R., *Proceedings of the 9th Conference on Coordination Chemistry*, p. 73. Bratislava—Smolenice, 1983.

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