

Table 2. Selected geometric parameters (Å, °)

Co—O(1)	2.132 (3)	C(4)—C(5)	1.376 (6)
Co—O(W1)	2.064 (3)	C(5)—C(6)	1.393 (8)
Co—O(W2)	2.072 (3)	C(6)—C(7)	1.367 (8)
O(1)—C(1)	1.260 (6)	C(7)—C(8)	1.375 (6)
O(2)—C(1)	1.268 (5)	C(8)—C(9)	1.397 (8)
C(1)—C(2)	1.530 (7)	C(9)—C(4)	1.385 (7)
C(2)—N(1)	1.449 (6)	C(7)—N(2)	1.486 (7)
N(1)—C(3)	1.333 (6)	N(2)—O(4)	1.190 (7)
C(3)—O(3)	1.240 (6)	N(2)—O(5)	1.219 (6)
C(3)—C(4)	1.500 (7)		
O(W1)—Co—O(W2)	91.4 (1)	C(3)—C(4)—C(5)	116.6 (4)
O(1)—Co—O(W2)	89.0 (1)	C(5)—C(4)—C(9)	120.0 (4)
O(1)—Co—O(W1)	89.7 (1)	C(4)—C(5)—C(6)	120.4 (5)
Co—O(1)—C(1)	129.0 (3)	C(5)—C(6)—C(7)	118.2 (5)
O(1)—C(1)—O(2)	124.5 (4)	C(6)—C(7)—N(2)	119.1 (5)
O(2)—C(1)—C(2)	118.1 (4)	C(6)—C(7)—C(8)	123.3 (5)
O(1)—C(1)—C(2)	117.4 (4)	C(8)—C(7)—N(2)	117.6 (5)
C(1)—C(2)—N(1)	112.5 (4)	C(7)—C(8)—C(9)	117.6 (5)
C(2)—N(1)—C(3)	119.1 (4)	C(4)—C(9)—C(8)	120.4 (5)
N(1)—C(3)—C(4)	118.4 (4)	C(7)—N(2)—O(5)	115.8 (5)
N(1)—C(3)—O(3)	121.2 (4)	C(7)—N(2)—O(4)	118.9 (4)
O(3)—C(3)—C(4)	120.4 (4)	O(4)—N(2)—O(5)	125.1 (5)
C(3)—C(4)—C(9)	123.3 (4)		

The structure was solved by conventional Patterson and Fourier techniques, and was refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. H atoms, except those of water molecules, were located on a Fourier difference map and were treated as fixed contributors. Data collection, cell refinement, data reduction: *CAD-4 Software* (Enraf-Nonius, 1989). Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976). Program(s) used to refine structure: *SHELX76*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Battaglia, L. P., Bonamartini-Corradi, A., Menabue, L., Saladini, M., Sola, M. & Battistuzzi Gavioli, G. (1985). *Inorg. Chim. Acta*, **107**, 73–79.
- Eichelberger, H. R., Majeste, R., Surgi, R., Trefonas, L., Good, M. & Karraker, D. (1977). *J. Am. Chem. Soc.* **101**, 616–617.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Forti, L., Menabue, L. & Saladini, M. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2955–2959.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Menabue, L., Saladini, M., Battaglia, L. P., Bonamartini-Corradi, A., Marcotrigiano, G. & Morini, P. (1987). *J. Crystallogr. Spectrosc. Res.* **17**, 313–321.

Morelock, M. H., Good, M. L., Trefonas, L. M., Karraker, D., Maleki, L., Eichelberger, H. R., Majeste, R. & Doodge, J. (1979). *J. Am. Chem. Soc.* **101**, 4858–4866.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

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Bis[tris(bipyridine)nickel(II)] Tris[dicyanoargentate(I)] Chloride *n*-Hydrate (*n* = 9)

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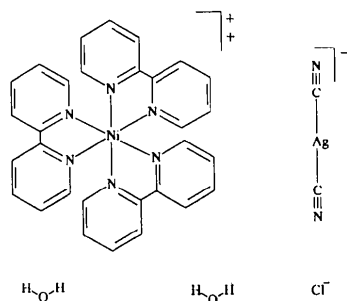
(Received 18 February 1994; accepted 19 May 1994)

Abstract

The structure of bis[tris(bipyridine)nickel(II)] tris[dicyanoargentate(I)] chloride nonahydrate, $[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)_3]_2[\text{Ag}(\text{CN})_2]_3 \cdot 9\text{H}_2\text{O}$, is ionic. It comprises $[\text{Ni}(\text{bpy})_3]^{2+}$ cations with threefold symmetry placed in the cavities of a three-dimensional hydrogen-bonded network formed by $\text{N}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ type contacts between linear $[\text{Ag}(\text{CN})_2]^-$ anions and a hexagonal prismatic cluster of water molecules formed by the packing of two crystallographically independent water molecules. The Cl^- anion is partially distributed over the positions of the O atoms. The Ni atom is in a six-coordinate N_6 deformed octahedral environment with the Ni—N distances being almost equal: 2.093 (3) (3 \times) and 2.096 (3) Å (3 \times). The Ag—C distance is 2.052 (5) Å.

Comment

This work forms part of a wider study of preparation, properties and structure of heterobimetallic cyanoargentate complexes (Černák, Gérard & Chomič, 1993; Chomič, Černák, Potočňák, Zvereva & Saveljeva, 1993). The title complex, (I), was prepared unexpectedly during our attempt to isolate the Ni(bpy)₃Ag₂(CN)₄·nH₂O complex. The measured IR spectrum and the results of control CHN analysis were in line with the desired composition (with *n* = 3), but the X-ray powder diffractogram of the product of thermal analysis indicated the presence of a small amount of AgCl as well as the expected NiO and Ag. The correct formula was established as [Ni(bpy)₃]₂[Ag(CN)₂]₃Cl·nH₂O with *n* = 9 (elemental analysis: calculated, C 45.77, H 3.84, N 14.56, Cl 2.05, Ni 6.78, Ag 18.69%; found, C 45.19, H 3.66, N 14.40, Cl 1.81, Ni 6.63, Ag 17.95%). In order to elucidate the structure, an X-ray analysis was undertaken. The details of preparation, identification and thermal properties will be given elsewhere (Chomič, Černák & Bálintová, 1994).



dicyanoargentate anion, which connects the individual clusters and so ensures the propagation of the network. The O2 atoms participate in three hydrogen bonds to O1 atoms. As a consequence, an extended three-dimensional hydrogen-bond network with large cavities is formed; the cations are placed in these cavities (Fig. 2). The structure of [Ni(en)₃][Ag(CN)₂]₂ (en = ethylenediamine) contains [Ni(en)₃]²⁺ cations similar in shape but smaller in size and the crystal packing does not require the pres-

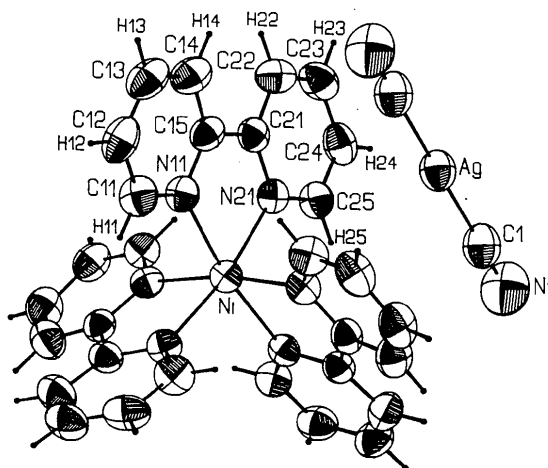


Fig. 1. An ORTEP (Johnson, 1965) view of the cation and anion along with atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

The structure of the title complex, (I), is ionic. The positive charge of two [Ni(bpy)₃]²⁺ cations (Fig. 1) in the unit cell is counterbalanced by three [Ag(CN)₂]⁻ anions and one Cl⁻ anion. There are two crystallographically independent sixfold positions for water molecules in the unit cell. These positions are partially occupied; the value of *n* = 9 for water content was found from the thermal analysis (found 9.5, calculated 9.36%). It is assumed that the Cl⁻ anion is distributed over the same positions as no other peak corresponding to this anion was found. A similar situation was found in the tartrate complex [Ni(bpy)₃](C₄H₄O₈)₂Cl·nH₂O (Wada, Katayama & Tanaka, 1976).

An interesting feature of this structure is the three-dimensional hydrogen-bond system formed by contacts of the O···O and O···N types (Table 2). The water molecules are placed around the corners of the unit cell so that they form a 'cluster' with a deformed hexagonal prismatic shape with $\bar{3}$ symmetry. The corners of these clusters are alternately occupied by O1 and O2 atoms. The O1 atoms form four hydrogen bonds; three to the neighbouring O2 atoms and one to the N atom from the

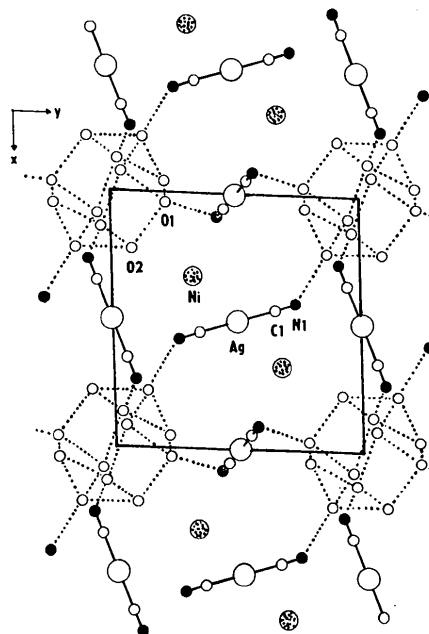


Fig. 2. A view of the proposed hydrogen-bonding system (Ugliendo, Borzani & Viterbo, 1988). For clarity, only the Ni atom is drawn for the cation. The possible hydrogen bonds are drawn as dotted lines.

ence of water molecules to fill the space (Kappenstein, Ouali, Guerin, Černák & Chomič, 1988). Considering these features it could be concluded that in the structure of the title complex the discrepancy between the size of the ions is compensated by the presence of water molecules and so better crystal packing is achieved. In addition, the hydrophobic character of the tris-bpy cation (only C—H bonds are directed outside the cation) could also have an effect. Similar hydrogen-bond systems are found in other cyanocomplexes, *e.g.* in the 5 K superconductor κ -[(BEDT-TTF)₂][Ag(CN)₂].H₂O, which has a two-dimensional network of the NC—Ag—CN···HOH···NC—Ag—CN type (Mori, Hirabayashi & Tanaka, 1991), and in the Cd(H₂O)₂Ni(CN)₄.4H₂O complex containing a two-dimensional ice structure of water molecules (Park, Kuroda & Iwamoto, 1993).

The Ni atom is pseudo-octahedrally coordinated by three bpy ligands, the chromophore being NiN₆. The observed bond lengths and angles are similar to the corresponding values found in [Ni(bpy)₃]SO₄·7.5H₂O (Wada, Sakabe & Tanaka, 1976).

The presence of short Ag···Ag distances is characteristic of many Ag complexes, *e.g.* in Ag₃(NSO₂)₃·3H₂O (3.032 Å; Dalgaard, Hazell & Hazell, 1974) or in Ag₄(NH₃)₅Mo(CN)₈·1.5H₂O [3.091 (1), 3.139 (1), 3.155 (1) Å; Meske & Babel, 1988]. This is not the case in the present complex as the shortest Ag···Agⁱ distance is 8.333 (2) Å [symmetry code: (i) z, x, y]. The Ag···Ni distance is shorter [4.815 (1) Å] but too long for any interaction. The bond distances in the [Ag(CN)₂]⁻ anion are normal (Zabel, Kühnel & Range, 1989).

Experimental

The compound was prepared according to the procedures of Chomič, Černák & Bálintová (1994). Suitable monocrystals were prepared by recrystallization of the microcrystalline product from a water–methanol mixture (1:2). The density, *D_m*, was measured by flotation in bromoform/acetone.

Crystal data

[Ni(C₁₀H₈N₂)₃]₂[Ag(CN)₂]₃Cl·9H₂O
M_r = 1731.84
 Trigonal
*R*3̄
a = 12.218 (2) Å
b = 12.218 (2) Å
c = 12.218 (2) Å
 α = 86.010 (10)°
V = 1811.2 (5) Å³
Z = 1
D_x = 1.588 Mg m⁻³
D_m = 1.56 Mg m⁻³

Data collection

Kuma KM-4 κ-axis diffractometer

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 9.47–10.66°
 μ = 1.410 mm⁻¹
T = 293 (2) K
 Pseudo cube
 0.4 × 0.35 × 0.35 mm
 Reddish violet

*R*_{int} = 0.0374
 θ_{max} = 29.99°

ω–2θ scans
 Absorption correction: none
 5989 measured reflections
 3526 independent reflections
 1737 observed reflections
 [*I* > 2σ(*I*)]

h = –17 → 0
k = –17 → 0
l = –17 → 17
 2 standard reflections monitored every 50 reflections
 intensity variation: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.0383
wR(*F*²) = 0.1121
S = 1.164
 3526 reflections
 149 parameters
 H-atom parameters not refined
w = 1/[σ²(*F_o*²) + (0.0717*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.024
 Δρ_{max} = 0.474 e Å⁻³
 Δρ_{min} = –0.243 e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ni	0.32499 (3)	0.32499 (3)	0.32499 (3)	0.0409 (2)
Ag	1/2	1/2	0	0.0634 (2)
O1†	0.0353 (5)	0.2225 (5)	0.8633 (5)	0.138 (2)
C11‡	0.0353 (5)	0.2225 (5)	0.8633 (5)	0.138 (2)
O2§	0.2195 (5)	0.0843 (4)	0.9517 (5)	0.148 (2)
C12¶	0.2195 (5)	0.0843 (4)	0.9517 (5)	0.148 (2)
N1	0.4253 (5)	0.7347 (4)	0.0893 (4)	0.102 (2)
C1	0.4536 (4)	0.6516 (4)	0.0568 (4)	0.0712 (11)
C11	0.2629 (3)	0.3287 (4)	0.0841 (3)	0.0608 (10)
C12	0.2095 (4)	0.3703 (4)	–0.0062 (3)	0.0679 (11)
C13	0.1594 (4)	0.4741 (4)	–0.0068 (3)	0.0714 (12)
C14	0.1682 (4)	0.5358 (4)	0.0831 (3)	0.0664 (10)
C15	0.2235 (3)	0.4898 (3)	0.1709 (3)	0.0493 (8)
N11	0.2688 (2)	0.3860 (2)	0.1729 (2)	0.0480 (7)
C21	0.2365 (3)	0.5492 (3)	0.2709 (3)	0.0467 (7)
C22	0.2101 (3)	0.6620 (3)	0.2762 (4)	0.0631 (10)
C23	0.2226 (3)	0.7110 (3)	0.3719 (4)	0.0644 (10)
C24	0.2596 (3)	0.6477 (3)	0.4608 (3)	0.0595 (9)
C25	0.2851 (3)	0.5370 (3)	0.4506 (3)	0.0509 (8)
N21	0.2756 (2)	0.4879 (2)	0.3565 (2)	0.0422 (6)

† Occupancy factor = 0.66.

‡ Occupancy factor = 0.07.

§ Occupancy factor = 0.84.

¶ Occupancy factor = 0.09.

Table 2. Selected geometric parameters (Å, °)

Ni—N21	2.093 (3)	C15—N11	1.347 (4)
Ni—N11	2.096 (3)	C15—C21	1.487 (5)
Ag—C1	2.052 (5)	C21—N21	1.339 (4)
N1—C1	1.138 (6)	C21—C22	1.398 (5)
C11—N11	1.340 (4)	C22—C23	1.373 (6)
C11—C12	1.370 (6)	C23—C24	1.374 (6)
C12—C13	1.369 (6)	C24—C25	1.379 (5)
C13—C14	1.389 (6)	C25—N21	1.348 (4)
C14—C15	1.374 (5)		
N21—Ni—N21 ⁱ	95.28 (10)	N21 ⁱⁱ —Ni—N11	92.37 (11)
N21—Ni—N11	78.46 (10)	N11 ⁱⁱ —Ni—N11	94.60 (10)
N21 ⁱ —Ni—N11	170.54 (11)	N1—C1—Ag	178.2 (5)

O1...O2	2.939 (8)	O1...O2 ^{iv}	2.937 (8)
O1...O2 ⁱⁱⁱ	2.818 (6)	O1...Ni ⁱ	2.930 (8)

Symmetry codes: (i) z, x, y ; (ii) y, z, x ; (iii) $z - 1, x, 1 + y$; (iv) $-y, 1 - z, 1 - x$.

The site occupation factors for O atoms were calculated using the value of the observed water content and the proportions derived from comparison of the electron-density peaks in the difference map [$K(O1) = 0.66, K(O2) = 0.84$]. The contribution of the Cl⁻ anion to the electron densities was assumed to be in the same proportions [$K(Cl1) = 0.07, K(Cl2) = 0.09$]. The H atoms from the bpy rings were placed in calculated positions assuming a riding model with $U(H) = 1.2U$ of the parent atom. No attempt was made to localize the H atoms of water molecules owing to partial occupancy and high displacement parameters.

Data collection, cell refinement and data reduction: KM-4 software. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Geometric analysis: *PARST* (Nardelli, 1983); *SHELXL93*. Molecular graphics: *ORTEP* (Johnson, 1965); *MOLDRAW* (Ugliendo, Borzani & Viterbo, 1988). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: KA1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Černák, J., Gérard, F. & Chomič, J. (1993). *Acta Cryst.* **C49**, 1294–1296.
- Chomič, J., Černák, J. & Bálintová, M. (1994). *Chem. Pap.* In preparation.
- Chomič, J., Černák, J., Potočňák, I., Zvereva, I. A. & Saveljeva, N. V. (1993). *Chem. Pap.* **47**, 175–178.
- Dalgaard, G. A. P., Hazell, A. C. & Hazell, R. G. (1974). *Acta Cryst.* **B30**, 2721–2724.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Kapfenstein, C., Ouali, A., Guerin, M., Černák, J. & Chomič, J. (1988). *Inorg. Chim. Acta*, **147**, 189–197.
- Meske, W. & Babel, D. (1988). *Z. Naturforsch. Teil B*, **43**, 1167–1173.
- Mori, H., Hirabayashi, I. & Tanaka, S. (1991). *Synth. Met.* **41**, 2255–2258.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Park, K. M., Kuroda, R. & Iwamoto, T. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 884–886.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Ugliendo, P., Borzani, G. & Viterbo, D. (1988). *J. Appl. Cryst.* **21**, 75.
- Wada, A., Katayama, C. & Tanaka, J. (1976). *Acta Cryst.* **B32**, 3194–3199.
- Wada, A., Sakabe, N. & Tanaka, J. (1976). *Acta Cryst.* **B32**, 1121–1127.
- Zabel, M., Kühnel, S. & Range, K.-J. (1989). *Acta Cryst.* **C45**, 1619–1621.

Acta Cryst. (1994). **C50**, 1566–1569

Hexakis(*N*-methylimidazol)-nickel(II)-bis(triiodid), [Ni(C₄H₆N₂)₆](I₃)₂†

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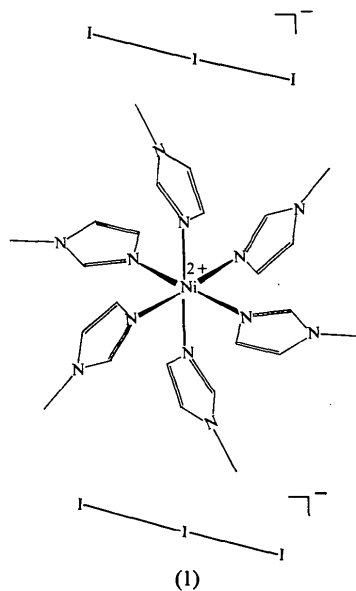
(Eingegangen am 22. September 1993; angenommen am 24. Januar 1994)

Abstract

The structure of the title compound consists of octahedrally coordinated centrosymmetric cations [Ni(C₄H₆N₂)₆]²⁺ and slightly asymmetric triiodide anions I₃⁻.

Kommentar

Komplexe Kationen sind zur Fällung von Polyiodidionen geeignet (Tebbe, 1977, und die dort zitierte Literatur). Hohe Koordinationszahlen und große Liganden sollten auch die Stabilisierung iodreicherer Polyiodidionen in Festkörpern ermöglichen. Mit diesem Ziel haben wir das Hexa(*N*-methylimidazol)-nickel(II)-Ion [Ni(NMIZ)₆]²⁺ ausgewählt und hiermit zunächst ein bisher unbekanntes Triiodid [Ni(NMIZ)₆](I₃)₂, (1), gewonnen.



Dieses kristallisiert salzartig im Formeltyp AB₂. Das koordinativ abgesättigte Zentralion Ni²⁺ besetzt eine Lage der Symmetrie $\bar{1}$ und hat insgesamt eine für Kom-

† Untersuchungen an Polyhalogeniden, 15. Teil 14: Tebbe & Kavosian (1994).