Preparation, Structure and Properties of Dicyano Silver Complexes of the M(en)$_3$Ag$_2$(CN)$_4$ and M(en)$_2$Ag$_2$(CN)$_4$ Type

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Abstract

Complexes of the M(en)$_3$Ag$_2$(CN)$_4$ (M = Ni, Zn, Cd) and M(en)$_2$Ag$_2$(CN)$_4$ (M = Ni, Cu, Zn, Cd) type were prepared and identified by elemental analysis, infrared spectroscopy, measurement of magnetic susceptibility, and X-ray powder diffractometry. The crystal structures of Ni(en)$_3$Ag$_2$(CN)$_4$ (I) and Zn(en)$_2$Ag$_2$(CN)$_4$ (II) were determined by the method of monocrystal structure analysis. Complex I crystallizes in the space group $C2/c$, $a = 1.2639(5)$, $b = 1.3739(4)$, $c = 1.2494(4)$ nm, $\beta = 113.25(4)°$, $D_m = 1.86(1)$, $D_c = 1.86$ g cm^{-3}, $Z = 4$, $R = 0.0429$. The crystal structure of I consists of complex cations [Ni(en)$_3$]$^{2+}$ and complex anions [Ag(CN)$_2$]$^-$. Complex II crystallizes in the space group $I2/m$, $a = 0.9150(3)$, $b = 1.3308(4)$, $c = 0.6442(2)$ nm, $\beta = 95.80(3)°$, $D_m = 2.14(1)$, $D_c = 2.15$ g cm^{-3}, $Z = 2$, $R = 0.0334$. Its crystal structure consists of infinite, positively charged chains of the [–NC–Ag–CN–Zn-(en)$_2$]$_n$$^{n+}$ type and isolated [Ag(CN)$_2$]$^-$ anions. The atoms of Ag are positioned parallely to the z axis and the Ag–Ag distance is equal to 0.3221(2) nm.

Introduction

With regard to the crystal structure, the cyano complexes of copper in mixed oxidation states represent an interesting class of compounds [1]. The results of structural analysis of the Cu(NH$_3$)$_2$-Cu$_2$(CN)$_4$ [2] and Cu(H$_2$O)(en)$_2$Cu$_2$(CN)$_4$ (en = 1,2-diaminoethane) [3] have shown that a complex polymer structure due to bridge-bonding of the cyano groups arises in both cases. This structure contains the Cu(I) atoms which show deformed trigonal-planar or tetrahedral coordination. Even in the 'simple' complexes, *i.e.* KCu(CN)$_2$ or NaCu-(CN)$_2$·2H$_2$O the Cu(I) atom is not coordinated linearly, but exhibits trigonal coordination [4, 5].

On the other hand, our knowledge of the crystal structure of dicyano silver complexes covers only the structure of KAg(CN)$_2$ in which the linear [Ag(CN)$_2$]$^-$ anions are present [6]. Recently the crystal structures of M[Ag$_2$(CN)$_4$]·2H$_2$O (M = Ca, Sr) with linear [Ag(CN)$_2$]$^-$ anions were solved [7]. A formation of chains of the Ag–CN–Ag–Ag–type was observed in the Ag$_3$(CN)(NO$_3$)$_2$ complex [8] and we may assume that it also occurs in AgCN [9]. On the basis of these facts, we can expect that the complexes of the common formula M(en)$_3$-Ag$_2$(CN)$_4$ or M(en)$_2$Ag$_2$(CN)$_4$ must exhibit other types of structure when compared with the above mentioned Cu(II)–Cu(I) complexes.

The aim of this study has been to describe the preparation and some properties of the complexes showing the following compositions: M(en)$_3$Ag$_2$-(CN)$_4$ (M = Ni, Zn, Cd) and M(en)$_2$Ag$_2$(CN)$_4$ (M = Ni, Cu, Zn, Cd) and on the basis of the results of structure analysis of two representatives of this group of complexes, *i.e.* Ni(en)$_3$Ag$_2$(CN)$_4$ and Zn(en)$_2$Ag$_2$(CN)$_4$ to point out some differences or similarities in crystallochemistry of the cyano silver and cyano copper(I) complexes and if need be of other cyano complexes. The thermal properties of these complexes were described in ref. 10.

Experimental

Synthesis and Analysis

The individual complexes were prepared by using 1 M solutions of Ni(NO$_3$)$_2$, NiAc$_2$ (Ac = CH$_3$COO$^-$), CuSO$_4$, Zn(Ac)$_2$, CdSO$_4$, Cd(Ac)$_2$, a 2 M solution of en (en = 1,2-diaminoethane) and a 0.4 M solution of KAg(CN)$_2$.

Ni(en)$_2$Ag$_2$(CN)$_4$ was prepared by mixing successively 5 cm^3 of the solution of Ni(NO$_3$)$_2$ with 5 cm^3 of the solution of en and 25 cm^3 of the solution of KAg(CN)$_2$. The molar ratio in this mixing was 1:2:2. The separated pink complex was sucked, washed with alcohol and ether, and dried in a desiccator over silica gel.

The colourless $Cd(en)_2Ag_2(CN)_4$ (we started from $CdSO_4$ solution) and $Zn(en)_2Ag_2(CN)_4$ (we started from $Zn(Ac)_2$ solution) complexes were prepared in a similar way. The $Zn(en)_2Ag_2(CN)_4$ complex was prepared so that the coagulate obtained by mixing the solutions was filtered off and the product, in the form of small crystals suited for X-ray analysis, separated from the filtrate in the course of 3 days.

$Ni(en)_3Ag_2(CN)_4$ was prepared by mixing 5 cm^3 of the solution of $Ni(Ac)_2$ with 25 cm^3 of the solution of en and 25 cm^3 of the solution of $KAg(CN)_2$. The molar ratios in this mixing were 1:10:2. Small violet crystals of the product crystallized in the form suitable for X-ray analysis in the course of 2–3 h from the violet solution. The crystals were sucked, washed with alcohol and ether and dried in a desiccator over silica gel.

The dark blue $Cu(en)_2Ag_2(CN)_4$ complex (we started from the solution of $CuSO_4$) and colourless $Cd(en)_3Ag_2(CN)_4$ complex (we started from $Cd(Ac)_2$) were prepared in an analogous way. The colourless $Zn(en)_3Ag_2(CN)_4$ was obtained by a similar procedure by using $Zn(Ac)_2$ and 50 cm^3 of the solution of en. Thus the molar ratio in mixing the solutions was 1:20:2.

The prepared complexes were analyzed with respect to the content of C, H, N, and metals. Carbon, hydrogen, and nitrogen were determined with an automatic CHN analyzer (Hewlett-Packard model 185). Gravimetry was applied to the determination of silver in the form of AgCl while other metals were determined by complexometry. The results of analyses are summarized in Table I. All prepared complexes are relatively stable, the evidence of decomposition starts to appear after a very long time (about one year) in the form of blackening due to reduced silver.

Physical Measurements

The infrared spectra were taken with instruments Specord 75 IR and Specord M 80 in the wavelength region 4000–200 cm^{-1} by using the KBr technique.

The magnetic susceptibilities were measured at laboratory temperature by the Faraday method.

The X-ray diffraction powder patterns were measured with an instrument Mikrometa II using Cu $K\alpha$ radiation.

X-ray Structure Analysis

For studying the structure of $Ni(en)_3Ag_2(CN)_4$ (I) a single crystal of pseudobipyramidal shape was selected. The exact lattice parameters were calculated by the method of least-squares from the angle coordinates of 15 precisely centered diffractions. On the basis of absences Cc or $C2/c$ were determined as possible space groups. The Patterson map was in line with the assumption that an atom of Ag occupies the common 8-fold position and, for this reason, the structure was solved in the $C2/c$ space group. The final results involving the correction of the experimental data showed that this choice was right. The density of crystals was measured by the immersion method in a bromoforme–acetone mixture. The basic crystallographic data as well as the experimental conditions of intensity measurements are given in Table II.

The structure was solved by the use of standard methods. The measured intensities were corrected for the Lorentz and polarization factors. On the basis of the three-dimensional map, the positions of the Ni and Ag atoms were found. The positions of other atoms were found by means of the difference Fourier synthesis. After refining the positions of atoms by the use of isotropic temperature factors, the value $R = 0.098$ was obtained ($R = \Sigma[F_o - |F_c|]/\Sigma F_o$). By introducing anisotropic temperature factors, the value of R was reduced to 0.0504. On this degree of refining we calculated the corrections for absorption which reduced R to 0.0464. Further decrease in the R factor was achieved by introducing the atoms of hydrogen the positions of which were calculated on the basis of stereochemical considerations. The final values were $R = 0.0429$ and $R_w = 0.0525$ where $R_w = [\Sigma w(F_o - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. In the course of refining the function $\Sigma w(F_o - |F_c|)^2$ ($w = 1/\sigma^2(F_o)$) was mini-

TABLE I. Analytical Data

Compound	C (%)		N (%)		N (%)		Ag (%)		M (%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$Ni(en)_2Ag_2(CN)_4$	19.19	19.27	3.60	3.23	22.51	22.47	42.53	43.26	11.57	11.77
$Cu(en)_2Ag_2(CN)_4$	18.84	19.08	3.73	3.20	22.51	22.25	42.65	42.85	12.37	12.62
$Zn(en)_2Ag_2(CN)_4$	19.04	19.01	3.97	3.19	22.19	22.17	42.49	42.69	12.94	12.93
$Cd(en)_2Ag_2(CN)_4$	16.84	17.39	3.14	2.91	20.68	20.28	39.18	39.06	20.60	20.35
$Ni(en)_3Ag_2(CN)_4$	21.18	21.49	4.25	4.32	25.28	25.06	38.28	38.61	10.44	10.55
$Zn(en)_3Ag_2(CN)_4$	20.50	21.23	4.29	4.27	24.55	24.76	38.11	38.15	11.75	11.56
$Cd(en)_3Ag_2(CN)_4$	19.16	19.60	4.49	3.94	22.61	22.86	35.37	35.22	18.33	18.35

TABLE II. Crystallographic Data and Experimental Conditions of Intensity Measurement

Compound	$Ni(en)_3Ag_2(CN)_4$	$Zn(en)_2Ag_2(CN)_4$
Molar weight (g mol^{-1})	558.82	505.38
Space group	$C2/c$	$I2/m$
Unit cell parameters (nm)		
a	1.2639(5)[a]	0.9150(3)
b	1.3739(4)	1.3308(4)
c	1.2494(4)	0.6442(2)
β	113.25(4)°	95.80(3)°
Volume of unit cell (nm^3)	1.9934(10)	0.7804(3)
Z	4	2
Density (g cm^{-3})		
D_m	1.86(1)	2.14(1)
D_c	1.862	2.151
μ(Mo Kα) (cm^{-1})	28.60	40.06
Shape and dimensions of	pseudobipyramide	plate
crystal (nm)	0.45 × 0.204 × 0.204	0.504 × 0.206 × 0.130
Crystal faces	$(\bar{1}11)$, $(1\bar{1}\bar{1})$, $(11\bar{1})$	(010), $(0\bar{1}0)$, $(\bar{1}01)$
	$(\bar{1}\bar{1}1)$, $(1\bar{2}0)$, $(\bar{1}20)$	$(10\bar{1})$, (110), $(1\bar{1}0)$
	(120), $(\bar{1}\bar{2}0)$	(110), $(\bar{2}0\bar{1})$
Diffractometer	CAD-4	CAD-4
Scanning technique	$\omega-2\theta$	$\omega-2\theta$
Radiation	Mo Kα	Mo Kα
λ (nm)	0.071069	0.071069
Monochromatization	graphite	graphite
Angle width	$(1.50 + 0.35 \text{ tg } \theta)°$	$(2.20 + 0.35 \text{ tg } \theta)°$
Range of scanning 2θ	2–60°	4–70°
Control of measurement	3 reflections measured always after 97 reflections	
No. measured reflections	3243	1969
Condition for observed reflection	$I > 2\sigma I$	$I > 2\sigma I$
No. observed reflection	1863	1355

[a]Number in parentheses gives standard deviation of the value presented in Table or text.

mized. The final difference map was without any marked maximum in the range $-1000 < \Delta\rho < 550$ e nm^{-3}.

For studying the structure of the $Zn(en)_2Ag_2$-$(CN)_4$ complex (II) a single crystal of the plate form was selected (Table II). Precise lattice parameters were obtained by refining the angle coordinates of 15 reflections. The density of crystals was determined by the immersion method as described earlier. On the basis of absences, it was ascertained that the space group was $C2$, $C2/m$ or even Cm. The centrosymmetric space group was confirmed by solving the structure. However, the refinement itself was carried out in the space group $I2/m$ [11] where the value of the angle β is nearer to 90°. The transformation matrix for the lattice parameters of the unit cell with the symmetry $C2/m$ ($a = 1.064$, $b = 1.330$, $c = 0.644$ nm, $\beta = 121.22$°) and lattice parameters of the unit cell with the symmetry $I2/m$ (Table II) has the form

$$S = \begin{pmatrix} 1 & 0 & 1 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$$

The basic crystallographic data and conditions of intensity measurements are given in Table II.

The measured intensities were corrected for the Lorentz and polarization factor. The positions of the Ag and Zn atoms were found by analysis of the Patterson map. Except hydrogen, other atoms were localized by the use of the difference Fourier synthesis. Successive refinements based on the method of least squares enabled us to obtain the value of the R factor equal to 0.0685. By introducing the correction for absorption the R factor was down to 0.482. The positions of the hydrogen atoms were calculated and involved in the last cycle of refinement but not refined. The final value of R factor was 0.0334 and that of the R_w factor 0.0390 ($w = 1/\sigma^2(F_o)$). The resulting difference Fourier map was within the limits $-2000 < \Delta\rho < 430$ e nm^{-3}.

For solving both structures we used the scattering factors corresponding to neutral atoms C, N, and H as well as to the Ag^+, Ni^{2+} or Zn^{2+} ions [12]. These factors were corrected for anomalous dispersion. All calculations were performed by means of the SHELX '76 programme [13] in the computation centres CICUP (Poitiers) and CIRCE (Orsay).

TABLE III. Position Parameters ($\times 10^4$) and Coefficients of Anisotropic Temperature Factors ($\times 10^4$ nm) of Atoms in Ni(en)$_3$-Ag$_2$(CN)$_4$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag	4227.1(4)	4462.9(4)	1086.4(4)	4.89(3)	6.27(3)	5.88(3)	−1.14(2)	1.67(2)	0.04(2)
Ni	0	3433.8(7)	2500	2.93(4)	3.45(5)	2.56(4)	0	0.90(3)	0
N(1)	1826(4)	5278(4)	952(5)	5.7(3)	6.2(4)	5.2(3)	0.5(3)	2.7(3)	0.1(3)
N(2)	6343(5)	3401(5)	813(6)	4.9(3)	8.4(4)	7.5(4)	−1.5(4)	1.4(3)	0.1(3)
N(11)	1195(4)	4617(3)	3108(4)	4.0(2)	4.2(3)	3.6(2)	−0.2(2)	1.5(2)	−0.3(2)
N(21)	270(4)	3332(3)	923(4)	5.1(3)	4.2(2)	3.3(2)	−0.2(2)	2.1(2)	0.7(2)
N(22)	1322(4)	2359(3)	3047(4)	3.5(2)	4.6(3)	4.0(2)	0.7(2)	0.1(2)	0.5(2)
C(1)	2708(5)	5013(4)	1046(5)	5.9(3)	4.0(3)	4.2(3)	−0.0(3)	2.3(3)	−0.1(3)
C(2)	5627(5)	3809(5)	961(6)	4.4(3)	6.4(4)	5.9(4)	−0.8(3)	1.2(3)	−0.3(3)
C(11)	547(5)	5507(4)	3061(5)	5.5(3)	3.8(3)	5.2(3)	−0.8(3)	2.2(3)	0.2(3)
C(21)	1332(5)	2767(4)	1161(5)	5.0(3)	4.8(3)	5.3(3)	−0.0(3)	2.8(3)	0.5(3)
C(22)	1404(5)	1932(4)	1989(6)	4.8(3)	4.1(3)	6.0(4)	−0.2(3)	2.0(3)	0.9(3)

TABLE IV. Position Parameters ($\times 10^4$) and Coefficients of Anisotropic Temperature Factors ($\times 10^4$ nm) in Zn(en)$_2$Ag$_2$(CN)$_4$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag(1)	0	0	0	2.89(2)	5.60(3)	4.14(2)	0	−1.10(1)	0
Ag(2)	0	0	5000	4.00(2)	5.53(3)	5.03(3)	0	−0.23(2)	0
Zn	5000	0	5000	3.03(3)	3.86(3)	4.86(4)	0	0.25(3)	0
N(1)	3299(4)	0	2106(6)	3.3(2)	6.0(2)	5.2(2)	0	−1.0(1)	0
N(2)	0	2390(4)	5000	9.3(4)	5.8(3)	5.1(3)	0	0.6(3)	0
N(11)	3832(3)	1211(2)	6254(4)	3.4(1)	5.2(1)	4.7(1)	−0.5(1)	−0.2(1)	0.3(1)
C(1)	2166(4)	0	1208(6)	3.3(2)	5.2(2)	3.8(2)	0	−0.6(1)	0
C(2)	0	1546(4)	5000	4.7(2)	6.1(3)	4.4(2)	0	0.2(2)	0
C(11)	4177(4)	2123(3)	5111(6)	5.9(2)	4.3(2)	5.4(2)	−0.4(1)	−0.9(2)	1.2(1)

The final fractional coordinates of atoms with anisotropic coefficients of temperature factors are presented for I in Table III and for II in Table IV. See also 'Supplementary Material'.

Results and Discussion

The crystal structure of Ni(en)$_3$Ag$_2$(CN)$_4$ exhibits ionic character and the building particles are the complex [Ni(en)$_3$]$^{2+}$ cations and the complex [Ag-(CN)$_2$]$^-$ anions (Fig. 1). The complex cations and anions are situated in bands parallel to the c axis. A band containing two complex cations for a unit of period is enveloped by four bands containing four complex anions per unit of period and vice versa. The least distance between the atoms of Ni and Ag is 0.5699(1) nm the others exceed 0.6 nm. The distances between the atoms of Ag which occur in one band are short. They constitute a broken figure with alternating distances 0.3293(2) and 0.4189(1) nm, the first of which corresponds to
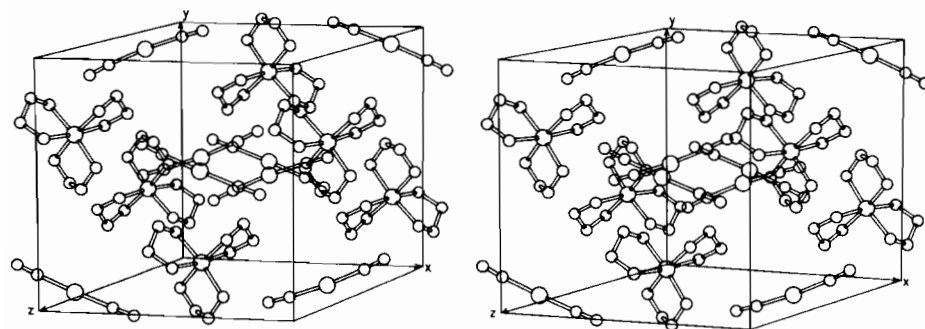
Fig. 1. Stereoscopic picture of the Ni(en)$_3$Ag$_2$(CN)$_4$ structure.

the limit of the assumed metal–metal interaction [14]. The smallest distance between two Ag atoms occurring in adjoining bands is equal to 0.6795(2) nm.

The Ni atom is coordinated in deformed octahedral form through chelate-bonded molecules of en (Fig. 2). The absolute configuration of the complex ion is $\Lambda\delta\lambda\lambda$ in contrast to the most stable $\Lambda\delta\delta\delta$ configuration [15]. This configuration may be explained as a consequence of the presence of strong hydrogen bonds of the NH...NC type (<0.31 nm) (Table V). The mean values of bond lengths (Table
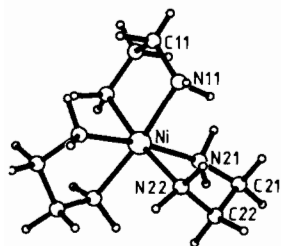

Fig. 2. View of the [Ni(en)₃]²⁺ cation in direction of pseudo-C_3 axis.

V) Ni–N 0.2136(7, 8)*, C–N 0.1474(12, 14) and C–C 0.1526(5, 6) nm are in good agreement with the values presented in the literature [3, 16].

As was expected the value of the N–Ni–N angle in the chelate ring (81.7(3, 3)°) is lower than the mean value of this angle outside the chelate ring (92.9(9, 1.2)°). Other angles in the chelate rings are near to the tetrahedral value.

The Ag atom is linearly coordinated by two cyano groups. A small but significant deviation from linearity may be due to the presence of hydrogen bonds of the NH...N type. The average value of the C≡N bond length (0.1137(3, 3) nm) is in agreement with the published data [17]. The Ag–C bond length (0.2045 nm) is in line with the data of other work [7–9], but it is shorter than that found for KAg(CN)₂ (0.213 nm) [6, 17].

The Zn(en)₂Ag₂(CN)₄ complex exhibits a different type of structure when compared with Ni-(en)₃Ag₂(CN)₄. The basis of the structure are infinite

*The first number in the parentheses gives standard deviation and the second one gives the maximum deviation from the mean value.

TABLE V. Interatomic Distances (nm) and Valency Angles (°) in Ni(en)₃Ag₂(CN)₄

Ni-octahedron			
Ni–N(11)	0.2144(4)	N(11)–Ni–N(11)^i	81.4(2)
Ni–N(21)	0.2133(4)	N(21)–Ni–N(22)	81.9(2)
Ni–N(22)	0.2130(4)	N(11)–Ni–N(22)	93.3(2)
		N(22)–Ni–N(22)^i	92.2(2)
		N(11)–Ni–N(21)	91.7(2)
		N(11)–Ni–N(21)^i	94.0(2)
		N(21)–Ni–N(22)^i	92.8(2)
1,2-Diaminoethane rings			
N(11)–C(11)	0.1460(7)	Ni–N(11)–C(11)	108.4(3)
C(11)–C(11)^i	0.1532(12)	N(11)–C(11)–C(11)^i	109.0(4)
N(21)–C(21)	0.1475(7)	Ni–N(21)–C(21)	108.2(3)
C(21)–C(22)	0.1523(8)	N(21)–C(21)–C(22)	109.8(4)
C(22)–N(22)	0.1487(8)	C(21)–C(22)–N(22)	107.5(4)
		C(22)–N(22)–Ni	108.0(3)
Dicyano silver anion			
Ag–C(1)	0.2045(6)	Ag–C(2)–N(2)	174.2(6)
Ag–C(2)	0.2045(7)	Ag–C(1)–N(1)	174.9(5)
C(1)–N(1)	0.1134(7)	C(1)–Ag–C(2)	173.1(2)
C(2)–N(2)	0.1140(8)		
Interaction Ag...Ag			
Ag.....Ag	0.3293(2)	Ag.....Ag	0.4189(1)
Hydrogen bonds			
N(11)–N(1)	0.3227(7)	N(21)...N(1)	0.3311(7)
N(11)–N(1)^{iv}	0.3323(7)	N(21)...N(1)^{ii}	0.3355(7)
N(11)–N(2)^i	0.3314(8)	N(21)...N(2)^{iii}	0.3322(8)
N(22)–N(2)^i	0.3077(8)		

Codes of symmetry: (i) $-x, y, 1/2 - z$; (ii) $-x, -y, -z$; (iii) $1/2 - x, 1/2 - y, -z$; (iv) $x, y - 1/2, z + 1/2$.
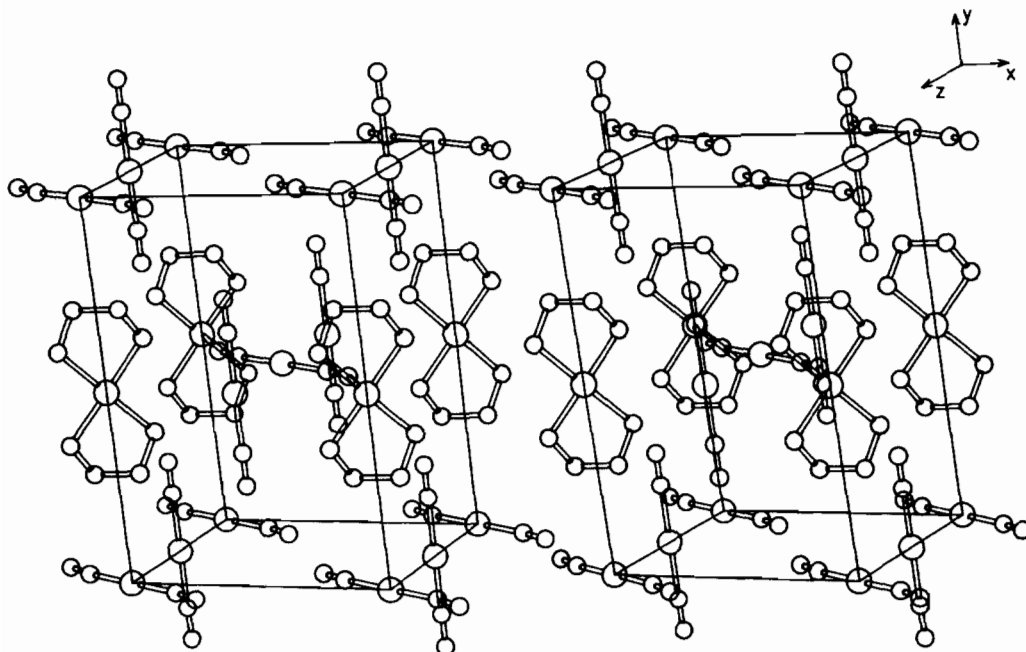
Fig. 3. Stereoscopic picture of the $Zn(en)_2Ag_2(CN)_4$ structure.

chains of the $[NC-Ag-CN-Zn(en)_2-]_n^{n+}$ type which proceed in the direction of the diagonal of the *ac* plane. Their positive charge is counterbalanced by the isolated $[Ag(CN)_2]^-$ anions (Fig. 3). Similar chains but electroneutral have been described in the case of the cyano complexes $Cu(en)_2Ni(CN)_4$ [18] and $Ni(en)_2Pd(CN)_4$ [19]. Covalent bonds operate within the chain. Ionic bonds and hydrogen bonds of the NH...N($\equiv$C) type work between chains and anions. The distance between the atoms of silver in the chain and in the anion is very small (0.3221(3) nm); in metallic silver this distance is equal to 0.289 nm [20]. Thus infinite Ag...Ag...Ag chains exhibiting metal—metal interaction arise in

TABLE VI. Interatomic Distances (nm) and Valency Angles ($^\circ$) in $Zn(en)_2Ag_2(CN)_4$

Zn-tetragonal bipyramide			
Zn–N(11)	0.2137(2)	N(1)–Zn–N(1)^i	180
Zn–N(1)	0.2305(4)	N(1)–Zn–N(11)	89.0(1)
		N(11)–Zn–N(11)^i	82.1(2)
1,2-Diaminoethane ring			
N(11)–C(11)	0.1470(4)	Zn–N(11)–C(11)	107.0(2)
C(11)–C(11)^i	0.1528(7)	N(11)–C(11)–C(11)^i	108.1(2)
Dicyano silver anions			
Ag(1)–C(1)	0.2054(4)	C(1)–Ag(1)–C(1)^{ii}	180
C(1)–N(1)	0.1135(5)	Ag(1)–C(1)–N(1)	171.7(4)
		C(1)–N(1)–Zn	156.9(4)
Ag(2)–C(2)	0.2057(5)	C(2)–Ag(2)–C(2)^{iii}	180
C(2)–N(2)	0.1124(7)	Ag(2)–C(2)–N(2)	180
Interaction Ag...Ag			
Ag(1)...Ag(2)	0.3221(2)	Ag(1)...Ag(2)...Ag(1)^{iv}	180
Hydrogen bond			
N(2)–N(11)	0.3148(4)		

Codes of symmetry: (i) $1 - x, y, 1 - z$; (ii) $-x, y, -z$; (iii) $x, -y, z$; (iv) $x, y, 1 - z$.

the direction parallel with the *c* axis. This interaction should manifest itself by increased conductivity of this complex.

The atom of Zn which occupies the special position b(2/m) is coordinated in the form of an extended tetragonal bipyramid because the axial Zn—N(C) bonds (0.2305(4) nm) are longer than the Zn—N(en) bonds (0.2137(2) nm) occurring in the equatorial plane. The molecules of en are bonded to give a chelate and occur in a left twisted-conformation. The bond lengths of C—N and C—C (Table VI) are equal in the range of standard deviation as ascertained for the $Ni(en)_3Ag_2(CN)_4$ complex. We can make a comparison of the bond length with the $[Zn(en)_3]^{2+}$ cation found in the compounds $Zn(en)_3Ni(CN)_4 \cdot H_2O$ and $Zn(en)_3Ni(CN)_4$ [21]. The mean bond length are displayed in Table VII and show that the bond lengths of the Zn—N bonds decrease by about 0.008 nm when one molecule of en is displaced from the coordination polyhedra. The strengthening of the Zn—N(en) bonds manifests itself by the higher temperature of departure of the en ligand. The lengths of the N—C bonds seem to show a slight decrease and the lengths of the C—C bonds a slight increase in the case of the $[Zn(en)_2]^{2+}$ cation. The same metal—N, N—C and C—C bond lengths can be found in the $[Ni(en)_3]^{2+}$ cation as in the $[Zn(en)_2]^{2+}$ cation. The valence angles in the chelate ring as well as the N—Zn—N angles do not exhibit any anomalies.

Two atoms of Ag in the structure which are not crystallographically equivalent are equally and linearly coordinated by two cyano groups. These cyano groups are one-functionally terminal in the isolated $[Ag(CN)_2]^-$ anion and the whole anion is exactly linear. However, that is not valid for the anion which is a component of the chain where the Ag—CN angle significantly deviates from linearity. Besides, a similar deviation was also observed in the structure of the Ni(II) complex. The (Ag)—C≡N—Zn angle with the value of 156.9(4)° is conspicuously deformed. This considerable deviation is, however, usual for some other cyano complexes, e.g. the value of that angle in the crystal structure of $Cn(en)_2Ni(CN)_4$ is even 123.1(5)° [18]. The observed values of the Ag—C and C≡N bond lengths (Table VI) are comparable with the lengths of the corresponding bonds in the structure of $Ni(en)_3$-$Ag_2(CN)_4$.

The measured infrared spectra (Fig. 4) are in line with the solved crystal structures. The characteristic sharp absorption bands due to the $\nu(C≡N)$ stretching

TABLE VII. Bond Lengths (nm) and Initial Temperature of the First en Ligand Liberation (°C) in $Zn(en)_2Ag_2(CN)_4$, $Zn(en)_3$-$Ni(CN)_4 \cdot H_2O$ and $Zn(en)_3Ni(CN)_4$

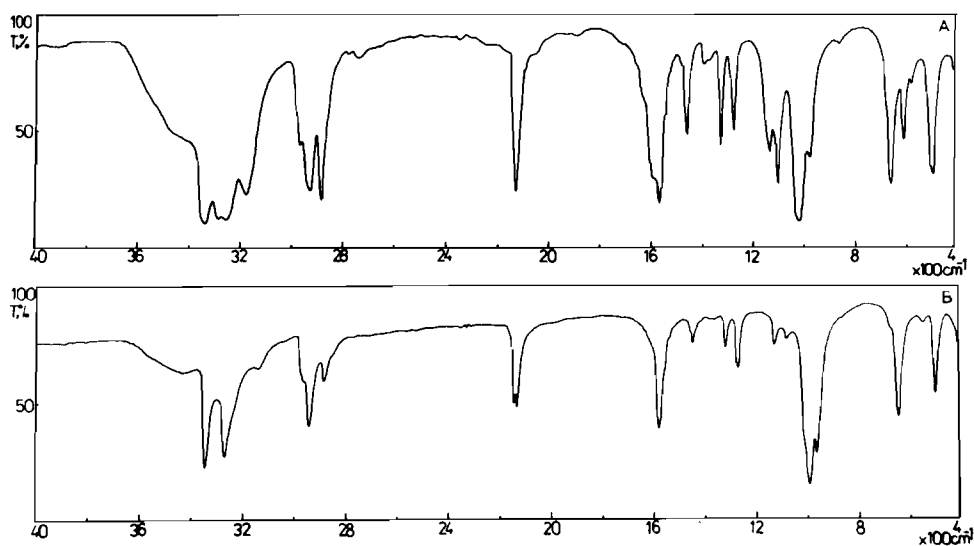| Compound	Zn—N(en)	N—C	C—C	t	Reference
$Zn(en)_2Ag_2(CN)_4$	0.2137(2)	0.1470(4)	0.1528(7)	182	this work, 10
$Zn(en)_3Ni(CN)_4 \cdot H_2O$	0.2223(24)	0.1530(61)	0.1496(33)	155	21, 22
$Zn(en)_3Ni(CN)_4$	0.2222(15)	0.1502(17)	0.1498(47)	155	21, 22

Fig. 4. The IR spectra of $Ni(en)_3Ag_2(CN)_4$ (A) and $Zn(en)_2Ag_2(CN)_4$ (B) in the region of 4000—400 cm^{-1}.

TABLE VIII. IR Spectra (in cm^{-1}) and Magnetic Moments (in BM)

Complex	$\nu(NH_2)$	$\nu(C\equiv N)$	$\delta(NH_2)$	$\nu(C-N)$	$\nu(C-C)$	$\rho(NH_2)$	$\delta(NCCN)$	$\nu(Ag-C)$	μ_{eff}
Ni(en)$_2$Ag$_2$(CN)$_4$	3344s 3272s 3153sh	2136s 2152s	1596s	1136m	1080m	664s	512m	392m	2.75
Cu(en)$_2$Ag$_2$(CN)$_4$	3329s 3249s 3125sh	2136s	1576vs	1152m	1084m	704s	532s	396s	1.79
Zn(en)$_2$Ag$_2$(CN)$_4$	3346s 3269s 3171s	2135s 2146s	1583s	1132w	1084w	647s	504s	396s	dia
Cd(en)$_2$Ag$_2$(CN)$_4$	3351s 3277s 3150sh	2135s 2141s	1581s	1124m	1092w	632s	488s	396s	dia
Ni(en)$_3$Ag$_2$(CN)$_4$	3337s 3284s 3253s 3179s	2127s	1590sh 1567s	1135m	1105s	657s	512s	396s	2.99
Zn(en)$_3$Ag$_2$(CN)$_4$	3350s 3316s 3279s 3179msh	2133s 2146sh	1573s	1102w	1086w	640m	496m	396m	dia
Cd(en)$_3$Ag$_2$(CN)$_4$	3353s 3328s 3275s 3173sh	2131s 2141sh	1577s	1102w	1080w, sh	616m	478s	394s	dia

vibration were observed in the spectra of all complexes. Only one such strong band was to be observed in the spectra of the tris(en) complexes in harmony with the one-functional binding of the cyano groups (Table VIII). In the case of the tris(en) complexes of Zn and Cd, however, a shoulder with higher wavenumbers was observed. Its observation by the activation of the Raman-active mode due to local symmetry perturbation could be explained. Two strong bands with equal intensity due to $\nu(CN)$ vibrations appeared in the spectra of the bis(en) complexes. The band at the higher value of wave number may thus correspond to the bridged cyano groups and the band at the lower value of wave number may be attributed to the terminal cyano groups. The Cu(en)$_2$Ag$_2$(CN)$_4$ complex represents an exception because it exhibited only one band in the pertinent region of the spectrum. However, this fact does not exclude the double mode of bonding of the cyano groups in the structure because only one absorption band of the $\nu(CN)$ type was observed in the spectrum of Cu(en)$_2$Ni(CN)$_4$ in spite of the presence of both terminal and bridged cyano groups in the structure of this complex [18, 23]. As showed by the results of the crystal structure analysis of the Cu(en)$_2$Ni(CN)$_4$ compound [18], the Cu–N($\equiv$C) distance (0.254(2)

nm) and Cu–N$\equiv$C angle (123.1(5)°) have unusual values. These showed that the Cu–N bond is weaker than for the others analogous complexes. Cu(en)$_2$Ag$_2$(CN)$_4$ probably exhibits a similar structure.

The presence of the molecules of en in all prepared complexes is evidenced by several characteristic absorption bands of the $\nu(NH)$, $\delta(NH_2)$ and $\rho(NH_2)$ types which are displayed in Table VIII. The absorption bands due to $\nu(C-H)$, $\delta(CH_2)$ and $\rho(CH_2)$ types are observed in the regions of 2850–3000(s), 1450(m) and 860(w, sh) cm^{-1}, respectively without any marked modification in the complexes studies. The chelate bonding of the molecules of en manifests itself by the medium or even strong absorption band due to the bending vibration of the chelate ring $\delta(N-C-C-N)$. This band occurs in the region of about 500 cm^{-1} [24] and its position is sensitive to the nature of the central atom M(II). The absorption bands due to the stretching vibrations $\nu(C-N)$ and $\nu(C-C)$ in the chelate ring are also displayed in Table VIII.

The coordination of the cyano groups gives rise to the absorption bands due to vibration $\nu(Ag-C)$ in the region of 396 cm^{-1} [25].

The measured values of magnetic moments (Table VIII) which show only small differences with the

pure spin values point out a pseudooctahedral co-ordination of the central Ni and Cu atoms which was confirmed in the structure of the $Ni(en)_3Ag_2(CN)_4$ complex.

All complexes were also studied by the method of X-ray powder diffraction. While an isomorphism of the tris(en) complexes was not confirmed which, however, did not exclude the existence of an equal type of structure of these complexes, the diffraction patterns of the bis(en) complexes are very similar. The existence of three very intensive peaks corresponding to the Miller indices 020, 040 and 060 is characteristic of the diffraction peaks of the bis(en) complexes. The noticeable intensity of these diffraction peaks may be explained by the fact that all heavy atoms existing in the structure of $Zn(en)_2Ag_2(CN)_4$ are placed in the (020) plane.

On the basis of the presented results obtained by indirect methods and stereochemical reasoning, we may assume that the structure of complexes of the $M(en)_3Ag_2(CN)_4$ type exhibits ionic character and the structure of complexes of the $M(en)_2Ag_2(CN)_4$ type is made up of the cationic chains of the mentioned type and isolated anions. The fact that we did not succeed in preparing the complex of the $Cu(en)_3Ag_2(CN)_4$ composition was evidently a consequence of the Jahn—Teller effect.

The crystal structures solved from a crystallo-chemical point of view have shown that a notice-able tendency to give rise to Ag...Ag interactions as observed in other silver complexes [7, 14, 20, 26] is also operating in the dicyano silver complexes. This tendency has not been observed in the case of copper(I) complexes due to the fact that essentially different types of complexes must be assumed. This observation is a manifestation of the differences in physical and chemical character of the Cu(I) and Ag(I) complexes.

Supplementary Material

Tables giving the calculated positions of the hydrogen atoms as well as the table with the structure factors are available from the authors on request.

Acknowledgements

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