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The Structure and Spectra of Bis(ethylenediamine)nickel(II)-Tetracyanopalladate(II), $Ni(NH_2CH_2CH_2NH_2)_2Pd(CN)_4$*

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The structure of bis(ethylenediamine)nickel(II)tetracyanopalladate(II),

$$Ni(NH_2CH_2CH_2NH_2)_2Pd(CN)_4,$$

has been determined from three-dimensional X-ray data, using Weissenberg photographs. The compound crystallizes with two molecules in the monoclinic space group $P2_1/n$ with a = 7.174(10), b = 10.740(15), c = 10.135(15) Å, $\beta = 115.0(5)°$. The measured and the calculated density is 1.83 g/cm³. Anisotropic refinement gave a final R factor of 10.2%. The structure consists of infinite chains,

–Pd–C–N–Ni–N–C–,

parallel to the c-axis. Two trans-nitrogen atoms of the square $Pd(CN)_4^{2-}$ are linked to Ni, leading thus to a polynuclear compound with an octahedral $[NiN_6]$ group in agreement with visible and infrared spectra. The trans-$Ni(NH_2CH_2CH_2NH_2)_2(NC)_2$-group has an asymmetric "gauche" ($\delta\lambda$)-conformation. Average distances are: Pd–C: 1.96 Å, C≡N: 1.15 Å, Ni–N: 2.08 Å.

Die Struktur von Bis(äthylendiamin)nickel(II)-tetracyanopalladat(II),

$$Ni(NH_2CH_2CH_2NH_2)_2Pd(CN)_4,$$

wurde mit Hilfe von Weissenbergaufnahmen ermittelt. Die Substanz kristallisiert mit zwei Formeleinheiten in der monoklinen Raumgruppe $P2_1/n$ mit den Zelldimensionen a = 7,174(10), b = 10,740(15), c = 10,135(15) Å, $\beta = 115,0(5)°$. Die gemessene und die berechnete Dichte betragen beide 1,83 g/cm³. Die Verfeinerung unter Berücksichtigung anisotroper Temperaturfaktoren führte zu einem R-Wert von 10,2%. Unendlich lange

–Pd–C–N–Ni–N–C–

Ketten sind parallel der c-Achse angeordnet. In Übereinstimmung mit den Spektren im sichtbaren und infraroten Bereich handelt es sich um einen polynuklearen Komplex, indem die trans-Cyanidgruppen von $Pd(CN)_4^{2-}$ als ambidente Liganden zu einer oktaedrischen $[NiN_6]$-Koordinationseinheit führen. Die trans-$Ni(NH_2CH_2CH_2NH_2)_2(NC)_2$-Gruppe weist eine asymmetrische „gauche" ($\delta\lambda$)-Konformation auf. Mittlere Atomabstände betragen: Pd–C = 1,96 Å, C≡N = 1,15 Å, Ni–N = 2,08 Å.

La structure du tétracyanopalladate (II) de bis (éthylènediamine) nickel (II) a été déterminée à partir de données tri-dimensionnelles aux rayons X, avec des photographies de Weissenberg. Le composé cristallise avec deux molécules dans le groupe spatial monoclinique $P2_1/n$ avec les paramètres a = 7.174 (10), b = 10.740 (15), c = 10.135 (15) Å, $\beta = 115.0\,(5)°$. La densité mesurée et calculée est 1,83 g/cm³. L'amélioration anisotrope donne un facteur R final de 10,2%. La structure se présente comme des chaînes infinies –Pd–C–N–Ni–N–C, parallèles à l'axe c. Deux atomes d'azote trans du groupe carré $Pd(CN)_4^{2-}$ sont liés à Ni, conduisant ainsi à un composé polycyclique avec un groupe

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* Dedicated to the memory of Professor Hans-Ludwig Schläfer.

[NiN_6] octaédrique, ce qui est en accord avec le spectre visible et infra-rouge. Le groupe trans-$Ni(NH_2CH_2CH_2NH_2)_2(NC)_2$ a une conformation assymétrique « gauche » ($\delta\lambda$). Les distances moyennes sont Pd–C: 1,96 Å, $C \equiv N$: 1,15 Å, Ni–N: 2,08 Å.

1. Introduction

The tetracyanometalates(II) of Ni, Pd, and Pt form well crystallized compounds with a variety of chelated metal diamine complexes. Crystals with a size of some mm can be easily grown from aqueous solutions containing the tetracyanometalate, a metal salt, and the diamine of the appropriate concentration ratio. With tris(ethylenediamine)-complexes,

$$M^A(en)_3^{2+}\ (M^A = Ni^{2+}, Zn^{2+}, Cd^{2+};\ en = NH_2CH_2CH_2NH_2),$$

rhombic plates of the composition

$$[M^A(en)_3]\,[M^B(CN)_4] \cdot H_2O,\ (M^B = Ni^{2+}, Pd^{2+}, Pt^{2+})$$

are obtained. These crystals contain discrete complex anions and cations. When the ethylenediamine concentration is lowered, monoclinic crystals of a pseudohexagonal prismatic habit are formed showing sharp extinction in the polarizing microscope. The analytical data give the formula $M^A(en)_2M^B(CN)_4$. Thus, these compounds may represent polynuclear complexes with ambident cyanide linkage, M^B–C–N–M^A. In this paper, the spectral and structural properties of the specific example $Ni(en)_2Pd(CN)_4$ will be described.

Strong evidence for ambident coordination by the cyanide ion is furnished by the infrared spectrum showing in particular two sharp absorption bands at 2119 and 2159 cm^{-1}. The former absorption corresponds to the stretching frequency of a terminal cyano group in the $Pd(CN)_4^{2-}$ complex [1]. The latter band is assigned to the same cyanide stretching mode for the case of carbon- and nitrogen-linkage, Pd–C–N–Ni [2].

The reflectance spectrum in the visible and ultraviolet region exhibits at high wavenumbers the typical three intense charge-transfer bands of the square $Pd(CN)_4^{2-}$ ion [3]. In the visible and near infrared part of the spectrum, three bands are observed, which are characteristic for octahedrally coordinated nickel [4]. The positions of the maxima (Table 1) correspond to the absorption maxima of a [NiN_6] unit. Furthermore, the existence of an octahedrally coordinated Ni complex in the lattice of $Ni(en)_2Pd(CN)_4$ is demonstrated by the magnetic moment of 3.1 Bohr magnetons per Ni^{2+}.

Table 1. *Reflectance spectrum of* $Ni(en)_2Pd(CN)_4$ *(kK)*

	[NiN_6]	$Ni(en)_3^{2+}$ [4]		[PdC_4]	$Pd(CN)_4^{2-}$ [3]
$^3T_{2g}$	11.4	11.2	$^1B_{1u}$	43.0	41.6
^1E_g	(12.0)	12.4	$^1A_{2u}$	45.5	45.4
$^3T_{1g}$	18.5	18.35	^1E_u	47.7	47.2
$^3T_{1g}$	(30.0)	29.0			

From the infrared and electronic spectra we conclude that this compound contains square $Pd(CN)_4^{2-}$ and octahedral $Ni(en)_2(NC)_2$ groups forming cyanide bridges Pd–C–N–Ni.

Distances M–C–N–M in the lattice of polynuclear cyanides are generally close to 5 Å [5]. Assuming the metals are in special crystallographic positions (cf. Sect. 2), a Pd–C–N–Ni bridge in the unit cell of $Ni(en)_2Pd(CN)_4$ can only occur along the *c*-axis. By combining the spectral data with the crystal geometry, the coarse structure of $Ni(en)_2Pd(CN)_4$ can be described as consisting of chains of –Ni–N–C–Pd– parallel to *c*, the needle-axis. Two additional cyanide ions complete the square planar coordination geometry of Pd^{2+} and two chelated ethylenediamine molecules are bonded to Ni^{2+} giving an octahedral $[NiN_6]$ unit.

2. Unit Cell Data and Collection of Intensities

On the basis of precession photographs taken with MoKα radiation, $Ni(en)_2Pd(CN)_4$ was assigned to the monoclinic system. Zero-level and upper-level zones had systematic extinctions $h0\ell$, when $h+\ell \neq 2n$ and $0k0$ when $k \neq 2n$. These extinctions are consistent with the space group $P2_1/n$. The transformation to the space group $P2_1/c$, conforming to the setting of the axes in the "International Tables" [6], was not made because of structural and morphological reasons. In $P2_1/n$ the *c*-axis coincides with the needle axis and with the direction of the Pd–C–N–Ni chain.

The unit cell dimensions were determined from high-angle reflections of Weissenberg zero-level photographs calibrated with silicon ($\lambda(\mathrm{CuK}\alpha_2) = 1.5443$ Å, $\lambda(\mathrm{CuK}\alpha_1) = 1.5405$ Å, $\lambda(\mathrm{CuK}\beta) = 1.3922$ Å, $a_0(\mathrm{Si}) = 5.4308$ Å): $a = 7.174(10)$ Å, $b = 10.740(15)$ Å, $c = 10.135(15)$ Å, $\beta = 115.0(5)^0$. With two formula units $Ni(en)_2Pd(CN)_4$ in the cell, the calculated density is 1.83 g/cm^3, which is in exact agreement with the observed value of 1.83 g/cm^3.

Integrated multiple film Weissenberg photographs (Ni-filtered CuKα radiation) were collected rotating the crystal around the *a*-axis (five layers) and around the *c*-axis (seven layers). Parts of the same cylindrical specimen of 0.2 mm diameter were used. Of the total of 1372 reflections 324 could not be recorded with the microdensitometer. These unobserved reflections were assigned half the intensity of the weakest reflection on the same set of films.

The intensity data were corrected for absorption (linear absorption-coefficient $\mu = 121.6\ \mathrm{cm}^{-1}$ for CuKα), Lorentz and polarisation factors using modified ICR-IBM-1620 programs [7]. After inter-film and inter-layer scaling the usual Wilson plot was applied to put the resulting $|F_0|$-values on an approximately absolute basis.

3. Solution and Refinement of the Structure

The spectral data and the geometrical considerations furnish enough information to construct a model (Fig. 1) to start the F_c-calculations.

The two Ni are placed at the special position $(0 0 \frac{1}{2}, \frac{1}{2} \frac{1}{2} 0)$, the two Pd at $(000, \frac{1}{2} \frac{1}{2} \frac{1}{2})$. The two angles φ_1 and φ_2 describing the positions of the coordination

Table 2. *Observed and calculated structure amplitudes (in electrons) for* $Ni(en)_2Pd(CN)_4$ *(asterisks Indicate unobserved reflections)*

H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)	H	K	L	F(O)	F(C)
0	2	0	140.5	150.7	7	2	1	8.2	11.4	-1	3	2	58.8	65.5	-2	2	3	21.9	22.4	-3	7	4	55.8	54.2	-5	7	5	4.0	2.9	0	1	7	24.8	22.8	-2	7	9	9.3	7.9
0	4	0	130.6	126.6	7	3	1	4.2	3.5	-1	4	2	5.2	4.1	-2	3	3	31.5	32.2	-3	8	4	5.5	4.2	-5	8	5	11.9	12.9	0	2	7	2.4	1.4 *	-2	8	9	1.9	3.2 *
0	6	0	73.6	72.8	7	4	1	7.3	8.6	-1	5	2	66.6	68.7	-2	4	3	6.2	1.5	-3	9	4	37.8	38.3	-5	9	5	2.9	2.1 *	0	3	7	23.5	23.8	-2	9	9	10.5	9.1
0	8	0	62.8	59.6	7	5	1	2.1	1.7 *	-1	6	2	6.0	3.2	-2	5	3	8.1	6.1	-3	10	4	2.5	0.7 *	-5	10	5	9.5	9.6	0	4	7	3.4	5.3	-2	0	10	39.4	41.4
0	10	0	51.7	50.8	7	6	1	5.6	7.1	-1	7	2	53.1	54.3	-2	6	3	4.6	3.4	-3	11	4	31.5	30.9	-6	1	5	21.1	21.2	0	5	7	22.9	21.0	-2	1	10	2.2	1.9 *
0	12	0	35.5	34.2	-1	0	1	12.4	8.1	-1	8	2	7.9	7.7	-2	7	3	8.8	4.6	-4	0	4	77.8	81.2	-6	2	5	2.9	1.6 *	0	6	7	2.2	1.1 *	-2	2	10	38.1	40.7
1	1	0	150.8	156.9	-1	1	1	9.5	8.6	-1	9	2	45.0	43.7	-2	8	3	6.7	6.6	-4	1	4	16.2	10.1	-6	3	5	12.2	11.9	0	7	7	12.4	15.0	-2	3	10	1.9	0.9 *
1	2	0	52.0	43.6	-1	2	1	49.7	60.2	-1	10	2	2.2	1.1 *	-2	9	3	17.8	17.2	-4	2	4	79.7	77.6	-6	4	5	2.2	1.1 *	0	8	7	1.9	0.6 *	-2	4	10	34.5	36.9
1	3	0	127.0	138.6	-1	3	1	33.1	37.3	-1	11	2	38.3	38.5	-2	10	3	4.5	4.5	-4	3	4	2.4	1.3 *	-6	5	5	12.2	13.7	0	9	7	8.0	7.5	-2	5	10	1.9	2.0 *
1	4	0	48.2	35.7	-1	4	1	10.5	6.4	-1	12	2	1.9	0.7 *	-2	11	3	7.7	7.7	-4	4	4	62.9	62.5	-6	6	5	1.9	0.5 *	0	10	7	1.7	3.7 *	-2	6	10	31.4	30.2
1	5	0	127.0	124.7	-1	5	1	4.9	5.4	-1	13	2	24.2	23.0	-2	12	3	1.7	1.3 *	-4	5	4	5.0	6.5	-6	7	5	5.7	6.8	0	11	7	4.3	8.4	-2	7	10	1.7	0.7 *
1	6	0	9.7	7.8	-1	6	1	11.5	10.4	-2	0	2	55.2	57.4	-2	13	3	10.2	10.0	-4	6	4	57.6	53.7	-6	8	5	1.7	0.8 *	0	0	8	43.9	44.7	-2	8	10	21.9	22.7 .
1	7	0	82.9	80.0	-1	7	1	16.4	14.6	-2	1	2	15.3	13.6	-3	0	3	16.4	14.5	-4	7	4	5.5	1.4	-6	9	5	6.5	5.8	0	1	8	3.6	0.8	-2	1	11	19.3	18.6
1	8	0	8.6	9.2	-1	8	1	16.0	18.1	-2	2	2	75.8	77.7	-3	1	3	16.5	18.9	-4	8	4	41.3	42.1	-6	10	5	1.1	1.1 *	0	2	8	44.3	44.5	-2	2	11	1.9	1.8 *
1	9	0	49.7	48.5	-1	9	1	7.1	6.5	-2	3	2	3.9	2.7	-3	2	3	17.7	18.0	-4	9	4	2.6	1.6 *	-7	0	5	17.0	17.3	0	3	8	2.4	0.2 *	-2	3	11	16.3	15.3
1	10	0	4.4	2.1 *	-1	10	1	15.3	13.8	-2	4	2	78.6	85.0	-3	3	3	9.8	9.0	-4	10	4	37.1	35.6	-7	1	5	2.2	2.7 *	0	4	8	34.5	34.5	-2	4	11	1.9	1.0 *
1	11	0	40.2	39.6	-1	11	1	6.2	6.5	-2	5	2	6.9	9.9	-3	4	3	35.3	36.7	-4	11	4	2.5	1.2 *	-7	2	5	9.3	9.2	0	5	8	2.4	1.9 *	-2	5	11	12.8	11.6
1	12	0	2.3	1.8 *	-1	12	1	12.0	9.8	-2	6	2	78.3	81.4	-3	5	3	1.7	0.8 *	-4	12	4	19.1	22.0	-7	3	5	2.5	1.9 *	0	6	8	26.7	26.9	-2	6	11	1.4	0.2 *
1	13	0	23.1	23.3	-2	1	1	9.9	7.5	-2	7	2	21.2	16.1	-3	6	3	18.8	20.4	-5	1	4	60.5	59.5	-7	4	5	11.7	11.1	0	7	8	3.5	4.6	-2	0	12	25.8	22.7
2	0	0	117.1	118.4	-2	2	1	19.6	18.0	-2	8	2	49.1	48.0	-3	7	3	6.3	4.9	-5	2	4	3.7	3.5	-7	5	5	5.5	5.8	0	8	8	25.0	23.9	-2	1	12	1.7	1.3 *
2	1	0	29.2	21.0	-2	3	1	11.2	15.2	-2	9	2	1.9	0.5 *	-3	8	3	18.1	17.7	-5	3	4	62.1	61.3	-7	6	5	8.9	9.2	0	9	8	1.9	3.7 *	-2	2	12	23.3	22.8
2	2	0	116.9	115.5	-2	4	1	3.2	0.3 *	-2	10	2	35.9	35.1	-3	9	3	9.5	11.1	-5	4	4	3.3	4.2 *	-7	7	5	1.7	0.5 *	0	10	8	17.7	19.0	-2	3	12	1.4	0.3 *
2	3	0	9.5	10.2	-2	5	1	19.2	21.9	-2	11	2	2.6	3.3 *	-3	10	3	10.5	8.0	-5	5	4	50.7	51.2	-7	8	5	6.9	6.3	0	1	9	7.6	8.2	-2	4	12	22.6	21.2
2	4	0	112.2	110.7	-2	6	1	17.4	18.1	-2	12	2	32.2	27.0	-3	11	3	3.2	3.1	-5	6	4	7.6	3.1	-8	1	5	7.1	5.6	0	2	9	2.3	1.7 *	3	0	7	16.3	16.4
2	5	0	21.3	16.5	-2	7	1	9.9	8.0	-3	1	2	80.2	81.5	-3	12	3	9.5	7.4	-5	7	4	42.2	43.3	-8	2	5	1.7	0.0 *	0	3	9	5.7	6.4	3	1	7	2.9	2.3 *
2	6	0	90.4	90.8	-2	8	1	7.9	7.2	-3	2	2	51.5	40.6	-4	1	3	20.3	18.6	-5	8	4	3.4	2.9 *	-8	3	5	8.1	7.8	0	4	9	2.0	0.9 *	3	2	7	14.9	13.8
2	7	0	2.4	2.3 *	-2	9	1	18.9	18.7	-3	3	2	80.2	75.3	-4	2	3	2.4	1.8 *	-5	9	4	35.2	35.0	-8	4	5	2.9	2.6	0	5	9	9.5	9.8	3	3	7	1.9	2.9 *
2	8	0	73.6	69.0	-2	10	1	2.0	0.1 *	-3	4	2	1.9	0.4 *	-4	3	3	19.5	18.4	-5	10	4	2.2	2.1 *	-8	5	5	9.0	9.0	0	6	9	1.9	1.4 *	3	4	7	13.5	13.2
2	9	0	12.7	11.5	-2	11	1	11.2	9.8	-3	5	2	62.2	62.2	-4	4	3	13.5	13.6	-5	11	4	20.5	20.7	-8	6	5	1.5	0.0 *	0	7	9	11.5	9.9	3	5	7	2.9	1.3 *
2	10	0	39.0	41.0	-2	12	1	4.3	4.1	-3	6	2	13.1	11.7	-4	5	3	19.1	21.4	-6	0	4	36.2	39.7	-9	0	5	5.9	5.7	0	8	9	1.8	1.6 *	3	6	7	14.4	12.3
2	11	0	2.0	2.0 *	-2	13	1	10.6	11.6	-3	7	2	55.2	54.8	-4	6	3	4.3	3.2	-6	1	4	4.0	2.5 *	-9	1	5	7.6	2.3	0	0	10	26.2	28.2	3	7	7	2.7	0.4 *
2	12	0	30.2	28.5	-3	0	1	9.5	9.7	-3	8	2	3.4	4.0	-4	7	3	21.4	24.0	-6	2	4	59.0	57.1	-9	2	5	2.0	6.6	0	1	10	6.1	2.6	3	1	8	40.9	31.2
3	1	0	106.8	107.1	-3	1	1	14.8	18.4	-3	9	2	40.4	40.5	-4	8	3	2.5	0.8 *	-6	3	4	4.8	4.6	0	0	6	100.8	81.6	0	2	10	28.9	30.3	3	2	8	1.9	0.2 *
3	2	0	9.5	12.3	-3	2	1	4.9	5.3	-3	10	2	2.4	1.5 *	-4	9	3	11.9	11.4	-6	4	4	49.3	44.2	0	1	6	4.8	2.1	0	3	10	5.3	4.1	3	3	8	32.1	25.3
3	3	0	106.5	101.0	-3	3	1	6.8	7.0	-3	11	2	37.3	29.8	-4	10	3	1.9	0.2 *	-6	5	4	2.9	1.2 *	0	2	6	59.6	77.2	0	4	10	29.2	27.9	3	4	8	1.7	3.0 *
3	4	0	13.2	9.9	-3	4	1	5.7	4.9	-3	12	2	2.3	2.7 *	-4	11	3	9.9	8.6	-6	6	4	38.3	38.0	0	3	6	7.6	6.2	0	5	10	5.9	4.2	3	5	8	22.2	19.1
3	5	0	70.8	70.1	-3	5	1	2.9	2.6 *	-4	0	2	84.7	82.2	-5	0	3	27.2	32.7	-6	7	4	2.6	2.7 *	0	4	6	54.6	62.2	0	6	10	22.2	23.7	3	6	8	1.0	0.8 *
3	6	0	5.1	7.0	-3	6	1	16.7	18.6	-4	1	2	2.3	1.3 *	-5	1	3	7.3	6.7	-6	8	4	28.3	29.9	0	5	6	2.7	2.9 *	0	7	10	1.9	1.7 *	3	0	9	9.4	7.5
3	7	0	60.0	59.6	-3	7	1	8.9	8.4	-4	2	2	78.9	76.2	-5	2	3	18.5	16.2	-6	9	4	2.5	1.6 *	0	6	6	45.2	48.4	0	1	11	15.4	11.3	3	1	9	1.3	0.0 *
3	8	0	11.9	11.0	-3	8	1	16.5	16.4	-4	3	2	2.2	2.6 *	-5	3	3	2.4	3.3 *	-6	10	4	20.2	21.5	0	7	6	2.9	3.6 *	0	2	11	2.2	1.2 *	3	2	9	8.1	7.4
3	9	0	44.8	45.0	-3	9	1	6.1	3.9	-4	4	2	60.1	60.2	-5	4	3	18.1	20.8	-7	1	4	41.9	41.9	0	8	6	37.9	37.3	0	3	11	13.8	11.6	-3	0	7	18.1	16.7
3	10	0	10.9	9.5	-3	10	1	14.5	13.4	-4	5	2	2.5	2.1 *	-5	5	3	3.5	8.0	-7	2	4	2.9	1.6 *	0	9	6	2.7	2.9 *	0	4	11	1.6	0.8 *	-3	1	7	4.5	4.0
3	11	0	32.0	31.9	-3	11	1	6.5	5.9	-4	6	2	43.3	43.3	-5	6	3	12.6	13.8	-7	3	4	36.3	37.6	0	10	6	35.2	32.0	1	0	7	36.7	33.9	-3	2	7	20.0	19.2
3	12	0	3.6	4.6	-3	12	1	7.2	8.5	-4	7	2	10.9	13.5	-5	7	3	6.7	3.3	-7	4	4	2.9	0.9 *	0	11	6	2.6	2.5 *	1	1	7	2.9	1.0 *	-3	3	7	3.0	1.9
4	0	0	88.4	89.0	-4	1	1	4.3	3.4	-4	8	2	39.5	39.0	-5	8	3	7.9	7.1	-7	5	4	27.9	28.4	1	1	6	53.3	61.7	1	2	7	19.6	18.1	-3	4	7	16.5	19.7
4	1	0	5.6	4.1	-4	2	1	2.9	1.3 *	-4	9	2	2.1	0.2 *	-5	9	3	2.6	2.7 *	-7	6	4	2.5	0.5 *	1	2	6	2.2	1.6 *	1	3	7	4.9	1.3	-3	5	7	3.0	6.0
4	2	0	79.0	79.7	-4	3	1	11.1	9.4	-4	10	2	30.1	30.3	-5	10	3	7.7	7.5	-7	7	4	25.5	25.6	1	3	6	55.3	64.0	1	4	7	18.1	17.5	-3	6	7	7.6	8.9
4	3	0	6.1	0.9	-4	4	1	9.8	11.3	-4	11	2	1.8	1.7 *	-5	11	3	1.6	1.0 *	-7	8	4	2.3	1.7 *	1	4	6	6.0	7.1	1	5	7	2.1	0.6 *	-3	7	7	2.9	4.3
4	4	0	72.1	70.9	-4	5	1	17.8	19.4	-4	12	2	18.3	19.8	-6	1	3	21.3	25.6	-8	0	4	28.6	27.5	1	5	6	45.7	47.6	1	6	7	11.5	14.5	-3	8	7	10.5	13.1
4	5	0	16.5	13.2	-4	6	1	2.9	0.9	-5	1	2	55.2	57.0	-6	2	3	4.9	2.2	-8	1	4	2.7	2.0 *	1	6	6	6.7	5.5	1	7	7	1.9	1.5 *	-3	9	7	6.5	4.2
4	6	0	42.3	42.0	-4	7	1	13.4	12.7	-5	2	2	2.1	0.0 *	-6	3	3	8.9	10.0	-8	2	4	27.6	27.9	1	7	6	40.6	42.8	1	8	7	11.0	11.3	-3	10	7	9.9	7.9
4	7	0	2.9	4.5 *	-4	8	1	2.9	2.9 *	-5	3	2	64.7	63.5	-6	4	3	7.2	5.7	-8	3	4	2.5	2.0 *	1	8	6	2.3	1.1 *	1	9	7	1.9	1.4 *	-3	11	7	2.6	2.8
4	8	0	44.0	43.4	-4	9	1	5.8	4.2	-5	4	2	2.2	0.5 *	-6	5	3	12.5	12.0	-8	4	4	26.0	26.6	1	9	6	26.4	32.3	1	10	7	7.5	10.1	-3	1	8	32.4	37.1
4	9	0	3.8	5.2 *	-4	10	1	4.6	4.1	-5	5	2	48.6	44.2	-6	6	3	2.9	3.6 *	-8	6	4	23.4	23.5	1	10	6	2.2	1.5 *	1	1	8	34.0	32.3	-3	2	8	3.0	5.8
4	10	0	32.0	32.4	-4	11	1	11.6	9.8	-5	6	2	2.2	0.2 *	-6	7	3	7.9	5.9	-9	1	4	23.4	21.2	1	11	6	16.7	22.4	1	2	8	3.6	3.5	-3	3	8	32.2	36.7
4	11	0	1.9	1.3 *	-5	0	1	21.7	27.6	-5	7	2	36.2	36.4	-6	8	3	2.9	1.3 *	0	1	5	13.0	16.0	2	0	6	37.3	40.9	1	3	8	38.8	37.1	-3	4	8	4.4	5.7
4	12	0	20.2	24.5	-5	1	1	11.6	12.1	-5	8	2	4.8	4.4	-6	9	3	8.6	8.2	0	2	5	1.9	0.4 *	2	1	6	4.1	0.6	1	4	8	2.2	0.6 *	-3	5	8	34.9	42.2
5	1	0	49.1	51.8	-5	2	1	11.2	9.2	-5	9	2	28.1	28.3	-6	10	3	2.0	1.1 *	0	3	5	15.3	20.5	2	2	6	66.3	53.2	1	5	8	30.6	30.6	-3	6	8	2.1	2.1 *
5	2	0	16.0	14.1	-5	3	1	4.2	3.2	-5	10	2	1.9	4.1 *	-7	0	3	11.2	10.3	0	4	5	9.8	12.0	2	3	6	5.7	5.7	1	6	8	1.9	2.7 *	-3	7	8	28.7	32.4
5	3	0	54.7	56.1	-5	4	1	6.7	4.7	-5	11	2	16.2	18.4	-7	1	3	4.0	2.6	0	5	5	16.7	16.2	2	4	6	39.7	45.6	1	7	8	28.0	28.3	-3	8	8	1.9	2.6 *
5	4	0	9.5	7.0	-5	5	1	2.3	2.5 *	-6	0	2	37.6	37.8	-7	2	3	7.7	5.5	0	6	5	2.6	3.8 *	2	5	6	2.0	0.2 *	1	8	8	1.7	5.0 *	-3	9	8	23.2	23.5
5	5	0	44.0	43.4	-5	6	1	9.9	6.1	-6	1	2	4.8	5.1	-7	3	3	6.2	5.1	0	7	5	20.2	21.4	2	6	6	37.6	41.1	1	9	8	21.0	20.9	-3	10	8	1.5	1.6 *
5	6	0	7.5	5.9	-5	7	1	3.8	3.9	-6	2	2	49.5	51.2	-7	4	3	12.8	14.0	0	8	5	5.3	5.0	2	7	6	1.9	1.7 *	1	0	9	9.7	8.8	-3	0	9	12.9	9.1
5	7	0	43.9	43.7	-5	8	1	8.4	4.1	-6	3	2	2.6	1.3 *	-7	5	3	3.8	4.0	0	9	5	14.3	13.5	2	8	6	33.4	35.4	1	1	9	2.0	1.7 *	-3	1	9	3.8	2.4
5	8	0	2.3	0.4 *	-5	9	1	2.0	0.2 *	-6	4	2	39.1	37.4	-7	6	3	11.5	12.7	0	10	5	1.9	0.7 *	2	9	6	1.8	1.7 *	1	2	9	7.1	4.7	-3	2	9	15.3	12.6
5	9	0	34.6	33.4	-5	10	1	12.4	9.1	-6	5	2	2.5	0.2 *	-7	7	3	4.8	3.1	0	11	5	10.5	9.7	2	10	6	20.4	23.4	1	3	9	1.9	1.3 *	-3	3	9	1.9	0.8 *
5	10	0	1.7	0.9 *	-6	1	1	11.6	8.4	-6	6	2	34.4	36.0	-7	8	3	10.5	10.3	0	12	5	3.9	5.0	3	1	6	38.5	39.5	1	4	9	8.6	9.1	-3	4	9	12.9	13.4
6	0	0	27.6	29.7	-6	2	1	4.8	4.1	-6	7	2	2.6	1.8 *	-8	1	3	6.7	6.2	1	0	5	26.1	32.8	3	2	6	2.9	3.3 *	1	5	9	1.7	1.6 *	-3	5	9	4.1	1.9
6	1	0	3.4	3.4 *	-6	3	1	6.5	3.7	-6	8	2	26.1	29.6	-8	2	3	3.9	5.2	1	1	5	1.9	1.6 *	3	3	6	38.0	41.4	1	6	9	12.5	9.1	-3	6	9	11.7	11.1
6	2	0	39.0	40.3	-6	4	1	3.9	5.5	-6	9	2	2.2	3.0 *	-8	3	3	9.8	10.0	1	2	5	12.2	18.3	3	4	6	10.7	4.7	1	7	9	1.4	0.1 *	-3	7	9	8.7	8.0
6	3	0	10.7	6.7	-6	5	1	12.8	11.9	-6	10	2	16.3	19.6	-8	4	3	1.8	1.5 *	1	3	5	9.8	9.2	3	5	6	30.9	34.0	1	1	10	21.7	22.6	-3	8	9	13.4	11.8
6	4	0	42.3	39.9	-6	6	1	3.1	2.3 *	-7	1	2	33.7	33.9	-8	5	3	8.9	8.2	1	4	5	13.6	21.4	3	6	6	2.5	1.7 *	1	2	10	1.7	0.4 *	-3	9	9	1.7	5.0 *
6	5	0	2.9	0.8 *	-6	7	1	9.1	6.1	-7	2	2	2.7	1.3 *	-8	6	3	1.6	0.0 *	1	5	5	2.9	3.6	3	7	6	28.3	28.3	1	3	10	27.6	25.1	-3	1	10	40.6	43.2
6	6	0	36.7	36.5	-6	8	1	2.7	4.3 *	-7	3	2	32.5	34.5	0	0	4	116.9	125.6	1	6	5	11.5	12.2	3	8	6	7.1	4.0	1	4	10	1.5	0.7 *	-3	2	10	2.1	0.4 *
6	7	0	2.7	3.7 *	-6	9	1	9.7	7.0	-7	4	2	2.6	4.2 *	0	1	4	21.3	20.5	1	7	5	2.9	4.1	3	9	6	22.9	23.3	1	5	10	21.0	21.7	-3	3	10	33.9	38.2
6	8	0	30.2	28.2	-7	0	1	8.6	4.7	-7	5	2	26.8	30.2	0	2	4	81.4	88.0	1	8	5	7.6	6.8	4	0	6	36.2	38.1	1	0	11	17.7	14.8	-3	4	10	1.8	1.8 *
6	9	0	2.2	4.1 *	-7	1	1	4.4	4.3	-7	6	2	2.2	2.0 *	0	3	4	1.9	1.0 *	1	9	5	2.7	2.0	4	1	6	2.6	2.6 *	-1	0	7	23.3	23.9	-3	5	10	31.5	36.0
7	1	0	34.6	35.3	-7	2	1	6.9	4.6	-7	7	2	23.5	24.1	0	4	4	66.3	74.2	1	10	5	9.5	9.3	4	2	6	32.5	33.1	-1	1	7	5.8	8.1	-3	6	10	1.6	0.5 *
7	2	0	5.5	1.8	-7	3	1	1.8	2.4 *	-8	0	2	30.0	30.5	0	5	4	2.0	1.5 *	1	11	5	1.5	0.7 *	4	3	6	2.4	0.9 *	-1	2	7	22.9	23.4	-3	7	10	29.0	29.5
7	3	0	27.3	27.5	-7	4	1	11.5	9.3	-8	1	2	2.2	1.3 *	0	6	4	59.6	61.6	2	1	5	25.2	28.1	4	4	6	25.1	26.6	-1	3	7	6.8	2.2	-3	8	10	1.3	1.3 *
7	4	0	3.0	3.0 *	-7	5	1	1.7	0.7 *	-8	2	2	25.8	26.9	0	7	4	2.3	0.4 *	2	2	5	6.8	7.5	4	5	6	2.2	0.5 *	-1	4	7	20.6	19.9	-3	0	11	17.0	17.1
7	5	0	20.4	22.8	-7	6	1	8.2	6.8	-8	3	2	2.2	1.2 *	0	8	4	51.4	47.8	2	3	5	10.2	8.1	4	6	6	21.5	21.5	-1	5	7	8.7	6.5	-3	1	11	1.8	1.0 *
7	6	0	2.4	0.6 *	-7	7	1	1.1	1.7 *	-8	4	2	21.2	21.5	0	9	4	2.6	2.1 *	2	4	5	4.1	5.0	4	7	6	3.9	2.3 *	-1	6	7	17.3	15.2	-3	2	11	16.3	16.5
7	7	0	18.6	19.5	-8	1	1	9.1	7.0	0	1	3	14.7	16.2	0	10	4	42.2	39.4	2	5	5	12.4	14.8	5	1	6	24.2	22.9	-1	7	7	3.4	2.7	-3	3	11	6.1	4.5
8	0	0	27.6	24.8	-8	2	1	1.7	2.1 *	0	2	3	1.7	1.7 *	0	11	4	1.8	1.6 *	2	6	5	3.8	3.9	5	2	6	7.6	3.7	-1	8	7	14.7	15.7	-3	4	11	14.0	12.7
8	1	0	3.8	3.5	-8	3	1	10.1	7.4	0	3	3	26.8	35.5	0	12	4	25.5	24.2	2	7	5	9.3	8.4	5	3	6	22.5	22.6	-1	9	7	3.0	5.5	-3	5	11	7.3	5.1

Table 2 (continued)

0	2	0	21.4	20.7	
0	3	0	1.9	1.9	*
0	1	1	15.1	17.3	
0	2	1	21.0	26.7	
0	3	1	43.3	55.3	
0	4	1	9.9	1.9	
0	5	1	14.8	13.4	
0	6	1	15.3	15.4	
0	7	1	25.7	27.9	
0	8	1	13.1	11.9	
0	9	1	15.6	16.1	
0	10	1	7.9	8.5	
0	11	1	8.6	7.7	
0	12	1	2.3	3.1	*
0	13	1	11.3	8.9	
1	0	1	12.5	7.5	
1	1	1	16.7	18.6	
1	2	1	44.7	52.7	
1	3	1	23.5	26.6	
1	4	1	27.6	31.4	
1	5	1	18.1	18.6	
1	6	1	25.5	30.4	
1	7	1	3.8	5.5	
1	8	1	15.3	17.6	
1	9	1	3.6	4.8	
1	10	1	14.7	13.0	
1	11	1	4.8	6.4	
1	12	1	8.6	7.2	
1	13	1	2.5	1.8	*
2	1	1	55.3	64.9	
2	2	1	9.9	11.6	
2	3	1	20.7	19.9	
2	4	1	16.5	18.5	
2	5	1	20.3	23.1	
2	6	1	3.3	2.7	
2	7	1	13.7	11.7	
2	8	1	3.4	4.6	
2	9	1	19.6	20.1	
2	10	1	2.2	4.9	*
2	11	1	9.7	9.7	
2	12	1	2.4	0.4	*
2	13	1	6.2	7.3	
3	0	1	24.9	27.0	
3	1	1	14.5	15.1	
3	2	1	32.7	35.8	
3	3	1	1.9	0.3	*
3	4	1	26.8	27.7	
3	5	1	2.7	1.9	*
3	6	1	25.2	30.3	
3	7	1	2.2	0.5	*
3	8	1	8.1	7.4	
3	9	1	3.4	5.3	
3	10	1	9.2	10.4	
3	11	1	2.0	0.0	*
3	12	1	8.6	7.6	
4	1	1	26.3	31.0	
4	2	1	3.8	2.2	
4	3	1	18.3	17.9	
4	4	1	2.2	2.4	*
4	5	1	19.6	21.6	
4	6	1	8.1	3.9	
4	7	1	14.8	17.4	
4	8	1	1.9	1.6	*
4	9	1	8.2	9.8	
4	10	1	2.7	0.5	
4	11	1	9.1	10.0	
5	0	1	20.0	19.3	
5	1	1	4.2	6.5	
5	2	1	17.0	16.5	
5	3	1	8.2	8.0	
5	4	1	15.3	16.4	
5	5	1	3.0	0.5	
5	6	1	16.0	19.1	
5	7	1	2.7	0.7	*
5	8	1	7.2	9.3	
5	9	1	3.3	2.8	*
5	10	1	8.4	9.9	
6	1	1	15.0	15.5	
6	2	1	3.6	3.9	
6	3	1	10.9	11.9	
6	4	1	3.3	2.4	*
6	5	1	9.3	12.8	
6	6	1	3.0	1.9	*
6	7	1	7.5	7.8	
6	8	1	1.9	1.5	*
6	9	1	8.6	9.4	
7	0	1	6.9	9.2	
7	1	1	2.6	0.4	*

-8	4	1	1.4	0.6	*
0	0	2	122.4	135.0	
0	1	2	10.9	6.7	
0	2	2	49.5	58.2	
0	3	2	30.1	29.6	
0	4	2	86.5	97.8	
0	5	2	5.7	3.8	
0	6	2	62.8	66.1	
0	7	2	7.2	4.6	
0	8	2	47.2	45.9	
0	9	2	7.6	5.1	
0	10	2	41.6	41.3	
0	11	2	1.9	1.7	*
0	12	2	29.5	30.6	
0	13	2	3.8	2.8	
1	1	2	75.3	81.5	
1	2	2	16.4	13.1	
1	3	2	67.6	75.0	
1	4	2	4.3	3.7	
1	5	2	67.1	71.9	
1	6	2	2.6	0.1	*
1	7	2	63.7	66.1	
1	8	2	9.9	10.0	
1	9	2	47.2	45.6	
1	10	2	1.9	0.1	*
1	11	2	33.9	33.7	
1	12	2	3.8	5.4	
1	13	2	21.4	20.2	
2	0	2	65.2	66.7	
2	1	2	24.4	18.4	
2	2	2	74.7	79.7	
2	3	2	3.9	2.2	
2	4	2	71.4	77.8	
2	5	2	21.1	12.7	
2	6	2	54.2	58.5	
2	7	2	15.3	12.3	
2	8	2	50.9	50.2	
2	9	2	2.5	1.2	*
2	10	2	29.3	30.0	
2	11	2	2.1	0.3	*
2	12	2	27.9	24.4	
3	1	2	74.2	78.4	
3	2	2	23.9	18.3	
3	3	2	75.5	76.3	
3	4	2	4.9	2.9	
3	5	2	48.0	46.9	
3	6	2	7.9	5.2	
3	7	2	39.1	39.9	
3	8	2	2.7	1.1	*
3	9	2	32.5	33.5	
3	10	2	3.9	3.7	
3	11	2	25.8	24.3	
4	0	2	67.0	66.7	
4	1	2	7.7	9.3	
4	2	2	58.0	55.5	
4	3	2	6.9	7.1	
4	4	2	51.4	53.0	
4	5	2	2.4	0.9	*
4	6	2	36.3	34.5	
4	7	2	5.9	4.7	
4	8	2	36.8	38.4	
4	9	2	7.2	6.6	
4	10	2	24.1	24.2	
5	1	2	36.8	37.5	
5	2	2	2.9	1.7	*
5	3	2	45.7	46.9	
5	4	2	5.9	6.8	
5	5	2	40.4	40.4	
5	6	2	2.7	0.5	*
5	7	2	31.4	34.6	
5	8	2	2.9	1.9	*
5	9	2	21.9	22.8	
6	0	2	41.1	39.5	
6	1	2	2.3	0.8	*
6	2	2	36.0	35.6	
6	3	2	5.4	5.7	
6	4	2	29.3	29.6	
6	5	2	3.7	2.7	
6	6	2	27.4	24.8	
6	7	2	1.9	1.3	*
6	8	2	20.0	20.7	
7	1	2	28.3	28.3	
7	2	2	1.9	2.2	*
7	3	2	23.2	23.3	
7	4	2	1.9	0.8	*
7	5	2	20.0	21.5	
-1	1	2	122.7	135.7	
-1	2	2	13.9	12.6	

0	4	3	2.0	3.0	*
0	5	3	23.8	26.6	
0	6	3	16.2	11.3	
0	7	3	25.3	30.0	
0	8	3	9.8	9.9	
0	9	3	16.9	14.3	
0	10	3	2.4	1.6	*
0	11	3	7.4	6.9	
0	12	3	2.0	2.9	*
0	13	3	6.9	6.9	
1	0	3	26.8	31.4	
1	1	3	10.2	7.3	
1	2	3	17.2	22.9	
1	3	3	10.5	13.9	
1	4	3	6.9	8.6	
1	5	3	14.8	8.2	
1	6	3	12.6	14.3	
1	7	3	6.7	7.2	
1	8	3	14.9	15.0	
1	9	3	7.0	6.5	
1	10	3	14.1	14.4	
1	11	3	4.5	3.1	
1	12	3	10.2	9.0	
1	13	3	3.9	3.5	
2	1	3	20.3	27.3	
2	2	3	10.2	9.7	
2	3	3	9.5	11.1	
2	4	3	2.0	3.5	*
2	5	3	17.2	21.3	
2	6	3	4.6	5.1	
2	7	3	4.6	3.2	
2	8	3	1.9	0.9	*
2	9	3	9.3	9.9	
2	10	3	2.3	0.9	*
2	11	3	11.2	11.0	
3	0	3	13.4	18.6	
3	1	3	9.5	10.7	
3	2	3	18.1	23.8	
3	3	3	4.5	2.5	
3	4	3	8.1	6.6	
3	5	3	7.0	8.5	
3	6	3	16.7	18.7	
3	7	3	2.7	0.9	*
3	8	3	11.9	9.1	
3	9	3	2.7	3.0	
3	10	3	11.2	11.5	
4	1	3	4.6	5.0	
4	2	3	2.4	2.5	*
4	3	3	7.7	9.4	
4	4	3	2.0	1.0	*
4	5	3	16.5	18.9	
4	6	3	4.8	4.3	
4	7	3	14.4	14.6	
4	8	3	1.8	0.0	*
4	9	3	7.2	7.2	
5	0	3	14.4	14.1	
5	1	3	8.6	9.2	
5	2	3	11.2	13.0	
5	3	3	5.7	5.2	
5	4	3	7.2	7.7	
5	5	3	1.9	2.1	*
5	6	3	7.9	8.1	
5	7	3	1.7	0.7	*
5	8	3	6.8	5.2	
6	1	3	11.5	12.3	
6	2	3	1.9	1.7	*
6	3	3	9.2	9.0	
6	4	3	2.0	3.3	*
6	5	3	5.6	5.7	
6	6	3	1.7	1.7	*
7	0	3	4.9	2.3	
7	1	3	1.7	0.0	*
7	2	3	8.6	8.1	
-1	0	3	13.1	13.2	
-1	1	3	50.1	57.6	
-1	2	3	44.0	46.4	
-1	3	3	24.8	24.6	
-1	4	3	24.5	24.0	
-1	5	3	20.1	23.6	
-1	6	3	11.5	10.6	
-1	7	3	6.2	6.2	
-1	8	3	17.8	19.2	
-1	9	3	6.1	1.6	
-1	10	3	9.5	9.1	
-1	11	3	1.9	0.7	*
-1	12	3	9.2	8.7	
-1	13	3	1.9	2.1	*
-2	1	3	59.4	60.9	

1	1	4	78.4	80.9	
1	2	4	7.6	6.6	
1	3	4	79.4	84.4	
1	4	4	9.6	8.2	
1	5	4	62.9	63.2	
1	6	4	3.3	2.6	*
1	7	4	54.3	52.7	
1	8	4	3.8	5.8	
1	9	4	38.5	36.2	
1	10	4	4.2	5.7	
1	11	4	26.3	27.0	
1	12	4	2.2	0.3	*
2	0	4	62.2	60.7	
2	1	4	19.8	14.6	
2	2	4	75.8	75.8	
2	3	4	2.9	1.8	*
2	4	4	62.1	61.7	
2	5	4	2.6	1.2	*
2	6	4	43.4	47.1	
2	7	4	7.6	4.6	
2	8	4	39.3	40.6	
2	9	4	2.3	2.1	*
2	10	4	26.0	26.2	
2	11	4	2.1	0.0	*
3	1	4	56.9	56.1	
3	2	4	4.8	4.5	
3	3	4	55.9	54.9	
3	4	4	4.8	4.1	
3	5	4	38.3	39.9	
3	6	4	3.2	0.2	*
3	7	4	36.9	37.5	
3	8	4	2.6	1.7	*
3	9	4	31.5	31.2	
3	10	4	1.9	0.1	*
3	11	4	20.3	19.9	
4	0	4	38.1	40.5	
4	1	4	3.3	1.9	*
4	2	4	40.6	39.4	
4	3	4	3.1	1.3	*
4	4	4	41.3	42.6	
4	5	4	2.9	1.7	*
4	6	4	29.1	31.2	
4	7	4	3.5	3.5	
4	8	4	26.5	28.3	
5	1	4	32.2	34.7	
5	2	4	3.3	2.0	*
5	3	4	28.3	30.8	
5	4	4	3.5	3.8	*
5	5	4	21.2	25.1	
5	6	4	2.3	1.4	*
5	7	4	23.8	23.4	
6	0	4	22.5	25.5	
6	1	4	2.0	1.3	*
6	2	4	19.4	22.9	
6	3	4	2.0	0.6	*
6	4	4	22.0	22.7	
-1	1	4	79.0	98.4	
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-1	3	4	86.8	85.7	
-1	4	4	5.5	5.5	
-1	5	4	93.2	91.2	
-1	6	4	4.2	2.7	
-1	7	4	59.5	57.2	
-1	8	4	3.1	2.3	*
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-1	10	4	2.9	1.5	*
-1	11	4	33.7	32.2	
-1	12	4	1.9	0.5	*
-1	13	4	20.5	20.4	
-2	0	4	115.3	110.5	
-2	1	4	5.0	2.8	
-2	2	4	101.2	103.3	
-2	3	4	6.1	9.6	
-2	4	4	70.1	70.3	
-2	5	4	10.5	7.2	
-2	6	4	76.3	75.1	
-2	7	4	2.9	1.6	*
-2	8	4	46.7	45.6	
-2	9	4	3.5	2.2	*
-2	10	4	40.2	38.3	
-2	11	4	2.5	0.8	*
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-3	6	4	7.6	7.6	

2	8	5	1.9	1.5	*
2	9	5	11.0	10.9	
2	10	5	1.9	2.4	*
2	11	5	9.5	9.5	
3	0	5	10.2	7.0	
3	1	5	3.3	4.8	
3	2	5	8.3	8.4	
3	3	5	2.5	1.2	*
3	4	5	15.3	15.6	
3	5	5	2.9	3.4	
3	6	5	17.0	19.4	
3	7	5	2.2	3.5	*
3	8	5	9.9	9.7	
3	9	5	1.7	1.0	*
3	10	5	6.4	7.3	
4	1	5	11.8	12.5	
4	2	5	8.1	9.1	
4	3	5	9.8	10.6	
4	4	5	1.9	1.5	*
4	5	5	9.8	10.3	
4	6	5	1.7	1.3	*
4	7	5	8.9	8.8	
4	8	5	3.5	2.9	
5	0	5	13.4	13.1	
5	1	5	1.7	0.8	*
5	2	5	10.7	11.9	
5	3	5	2.5	2.3	*
5	4	5	7.9	7.0	
5	5	5	1.7	1.4	*
5	6	5	4.8	4.6	
6	1	5	5.7	5.6	
6	2	5	1.2	1.1	*
-1	0	5	4.0	1.7	
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-1	2	5	11.9	17.0	
-1	3	5	3.6	4.2	
-1	4	5	22.9	27.1	
-1	5	5	6.0	7.8	
-1	6	5	17.8	19.8	
-1	7	5	2.2	3.7	*
-1	8	5	21.2	23.1	
-1	9	5	3.5	3.8	
-1	10	5	10.5	9.6	
-1	11	5	1.7	0.6	*
-1	12	5	9.5	8.5	
-2	1	5	25.2	30.4	
-2	2	5	18.6	16.8	
-2	3	5	26.1	29.5	
-2	4	5	9.7	11.1	
-2	5	5	10.8	10.4	
-2	6	5	2.5	0.0	*
-2	7	5	11.0	10.1	
-2	8	5	3.6	2.3	
-2	9	5	15.8	15.8	
-2	10	5	1.8	1.0	*
-2	11	5	9.3	9.6	
-2	12	5	1.7	0.7	*
-3	0	5	33.6	35.1	
-3	1	5	16.5	19.6	
-3	2	5	25.1	23.9	
-3	3	5	10.2	10.2	
-3	4	5	19.1	21.5	
-3	5	5	3.0	2.6	*
-3	6	5	7.3	6.8	
-3	7	5	2.9	2.5	
-3	8	5	17.8	18.0	
-3	9	5	6.0	6.2	
-3	10	5	9.7	9.8	
-3	11	5	1.7	0.9	*
-3	12	5	9.3	9.1	
-4	1	5	7.3	5.4	
-4	2	5	8.3	6.7	
-4	3	5	25.7	24.4	
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-4	6	5	4.8	5.3	
-4	7	5	20.6	22.0	
-4	8	5	1.9	0.9	*
-4	9	5	10.8	9.5	
-4	10	5	1.9	1.8	*
-4	11	5	7.9	8.6	
-5	0	5	23.1	25.7	
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-5	3	5	9.9	8.1	
-5	4	5	15.3	14.8	
-5	5	5	5.2	5.0	
-5	6	5	13.4	14.2	

5	4	6	2.0	0.7	*
-1	1	6	71.7	86.6	
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-1	3	6	101.5	66.6	
-1	4	6	8.7	1.6	
-1	5	6	59.0	64.9	
-1	6	6	8.6	0.9	
-1	7	6	58.2	49.8	
-1	8	6	9.1	5.3	
-1	9	6	40.9	40.4	
-1	10	6	7.6	4.8	
-1	11	6	29.1	27.9	
-1	12	6	1.7	0.7	*
-2	0	6	63.5	66.5	
-2	1	6	5.1	2.2	
-2	2	6	73.7	75.9	
-2	3	6	5.0	6.8	
-2	4	6	68.6	73.8	
-2	5	6	2.6	3.9	*
-2	6	6	87.7	72.6	
-2	7	6	2.4	0.4	*
-2	8	6	40.6	41.6	
-2	9	6	2.1	0.1	*
-2	10	6	32.4	32.0	
-2	11	6	4.5	1.9	
-2	12	6	17.9	21.5	
-3	1	6	99.2	92.8	
-3	2	6	20.0	15.6	
-3	3	6	68.0	67.8	
-3	4	6	6.7	2.7	
-3	5	6	58.0	60.1	
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-3	7	6	45.2	45.4	
-3	8	6	6.7	6.3	
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-3	11	6	27.3	27.9	
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-4	2	6	79.5	71.9	
-4	3	6	16.4	13.3	
-4	4	6	57.4	58.6	
-4	5	6	9.6	4.1	
-4	6	6	47.9	47.7	
-4	7	6	14.3	1.0	
-4	8	6	28.3	33.9	
-4	9	6	2.3	1.3	*
-4	10	6	32.8	30.0	
-4	11	6	8.6	1.5	
-5	1	6	59.1	55.0	
-5	2	6	9.1	1.6	
-5	3	6	54.6	54.5	
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-5	5	6	47.4	58.4	
-5	6	6	9.1	3.9	
-5	7	6	37.3	39.2	
-5	8	6	9.1	0.4	
-5	9	6	32.8	32.3	
-5	10	6	2.3	1.6	*
-5	11	6	11.6	20.1	
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-6	1	6	2.9	2.8	*
-6	2	6	51.9	47.7	
-6	3	6	2.7	0.1	*
-6	4	6	43.9	41.9	
-6	5	6	2.6	0.8	*
-6	6	6	35.0	37.7	
-6	7	6	2.4	1.4	*
-6	8	6	30.6	31.7	
-6	9	6	2.3	3.3	*
-6	10	6	15.6	20.3	
-7	1	6	40.2	38.6	
-7	2	6	8.7	3.0	
-7	3	6	36.3	37.7	
-7	4	6	1.9	1.6	*
-7	5	6	26.7	27.2	
-7	6	6	1.8	1.5	*
-7	7	6	22.3	22.6	
-7	8	6	3.9	4.1	
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-8	2	6	28.3	28.0	
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-8	4	6	24.6	23.3	
-8	5	6	1.9	1.4	*
-8	6	6	15.9	18.5	
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-9	2	6	1.9	2.5	*

-1	10	7	10.2	9.1	
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-1	8	9	7.3	7.1	
-1	1	10	36.5	38.9	
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-1	3	10	32.0	35.0	
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-1	5	10	23.3	28.5	
-1	6	10	1.9	3.5	*
-1	7	10	20.0	23.1	
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-1	1	11	2.9	2.2	*
-1	2	11	16.0	13.6	
-1	3	11	2.4	2.4	*
-1	4	11	14.3	13.0	
-1	5	11	1.5	0.8	*
-1	6	11	13.9	13.0	
-1	1	12	22.5	20.9	
-1	2	12	1.3	0.9	*
2	1	7	17.8	16.4	
2	2	7	3.2	2.2	
2	3	7	17.2	14.2	
2	4	7	2.7	2.4	*
2	5	7	20.8	19.8	
2	6	7	1.9	0.0	*
2	7	7	15.3	13.0	
2	8	7	2.3	0.8	*
2	9	7	8.3	9.7	
2	0	8	29.8	26.4	
2	1	8	5.0	2.8	
2	2	8	34.3	32.8	
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2	4	8	32.1	29.5	
2	5	8	6.7	4.8	
2	6	8	29.5	25.2	
2	7	8	1.5	0.1	*
2	1	9	13.4	10.3	
2	2	9	1.9	2.7	*
2	3	9	9.2	6.1	
2	4	9	1.8	0.9	
2	5	9	10.0	6.0	
2	0	10	23.1	21.7	
2	1	10	1.2	0.7	*
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-2	2	7	2.2	2.0	*
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-2	4	7	4.2	6.4	
-2	5	7	13.4	14.7	
-2	6	7	2.6	0.2	*
-2	7	7	13.4	14.8	
-2	8	7	2.5	3.5	*
-2	9	7	10.9	12.9	
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-2	6	8	34.5	38.9	
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-2	10	8	23.8	22.3	
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-2	3	9	10.5	11.8	
-2	4	9	2.5	0.9	*
-2	5	9	8.0	6.7	
-2	6	9	3.6	3.7	

-3	6	11	12.6	9.5	
-3	7	11	1.1	1.4	
-3	1	12	24.9	23.8	
-3	2	12	1.5	0.6	*
-3	3	12	24.6	22.3	
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-3	5	12	21.1	19.7	
4	1	7	17.2	13.1	
4	2	7	3.8	0.2	
4	3	7	17.7	12.0	
4	4	7	5.6	2.9	
4	5	7	9.9	9.0	
4	0	8	28.1	21.6	
4	1	8	2.7	2.6	
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-4	7	7	8.8	13.6	
-4	8	7	2.7	2.7	*
-4	9	7	8.3	8.6	
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-4	11	7	5.6	7.1	
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-4	4	8	30.0	32.9	
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-4	6	8	26.9	27.5	
-4	7	8	2.2	1.2	*
-4	8	8	22.5	22.5	
-4	9	8	1.9	0.7	*
-4	10	8	23.0	21.7	
-4	1	9	17.4	18.5	
-4	2	9	3.8	4.9	
-4	3	9	20.1	17.9	
-4	4	9	4.2	7.5	
-4	5	9	13.4	12.9	
-4	6	9	2.3	4.8	*
-4	7	9	9.6	12.7	
-4	8	9	2.1	3.0	*
-4	9	9	7.5	7.8	
-4	0	10	44.8	45.8	
-4	1	10	4.8	1.6	
-4	2	10	38.6	40.0	
-4	3	10	3.0	1.0	*
-4	4	10	33.3	38.3	
-4	5	10	2.9	2.2	*
-4	6	10	29.7	32.3	
-4	7	10	6.3	0.1	
-4	8	10	21.3	23.4	
-4	1	11	9.5	9.3	
-4	2	11	3.8	3.1	
-4	3	11	13.8	13.6	
-4	4	11	3.0	4.1	*
-4	5	11	13.4	12.6	
-4	6	11	2.7	2.5	*
-4	7	11	11.5	12.5	
-4	0	12	28.8	24.7	
-4	1	12	2.7	1.8	*
-4	2	12	27.4	21.4	
-4	3	12	2.5	1.7	*
-4	4	12	21.5	19.4	
-4	5	12	1.8	1.5	*

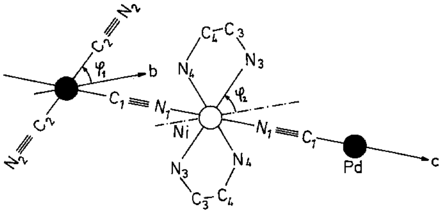

Fig. 1. Essential features of the structure model of $Ni(en)_2Pd(CN)_4$

polyhedra with respect to the crystallographic *b*-axis are the first parameters to be determined. Inserting known values of bond lengths [8, 9] and assuming a linear Pd–C–N–Ni chain a Monte Carlo calculation was made to obtain the values of φ_1 and φ_2. This calculation gave minimal *R*-factors for the following values of these two angles: φ_1: 22/67/115/165°, φ_2: 22/65/120°. The results of this first approximation were used to calculate Fourier and difference Fourier syntheses.

The structure factor and Fourier calculations were carried out on a GE-BULL-Gamma 30 computer. ICR-programs were used in a modified version [7].

The atomic scattering factors tabulated in the "International Tables" [10] were used for C, N, N^{-1}, Ni^{2+}, and Ru (same number of electrons as Pd^{2+}). The effect of anomalous dispersion was neglected. The positions of all nonhydrogen atoms could be obtained by interpreting difference Fourier maps. The positional as well as the isotropic and anisotropic thermal parameters were subjected to a least-squares refinement using a block-matrix notation. The function minimized was $\sum \sqrt{w}\,(|F_0| - |F_c|)^2$, where the weighting function is given by

$$w = \left(2|F_{\min}| + |F_0| + \frac{2|F_0|^2}{|F_{\max}|}\right)^{-1}, \quad |F_{\min}| = 1.1,\ |F_{\max}| = 158.7\,.$$

F_0 and F_c are the observed and calculated structure factors, respectively. The refinement converged to a value of *R* of 10.2%, where $R = \sum \| F_0| - |F_c\| / \sum |F_0|$.

In Table 2 are listed the final values of $|F_0|$ and $|F_c|$ in electrons. Table 3 lists the corresponding atomic and thermal parameters and Table 4 the root-mean-square amplitudes of the thermal vibration.

4. Description of the Structure

The crystal structure of $Ni(en)_2Pd(CN)_4$ consists of electrically neutral infinite $-N-C-Pd(CN)_2-C-N-Ni(en)_2-N-C-$ chains parallel to the *c*-axis. The packing of the octahedral $[NiN_6]$ and square $[PdC_4]$ coordination units is shown in Fig. 2. Fig. 3 illustrates the arrangement of the nonhydrogen atoms in a projection of the unit cell on the (010)-plane.

The metal-cyanide-chains are assumed to be connected by hydrogen bonds between the amino groups and the terminal cyanide ions. The corresponding N–N distances are 3.26(1) Å (N(2)–N(3)) and 3.32(1) Å (N(2)–N(4)). The observed

Table 3. *Positional and thermal parameters for* Ni(en)$_2$ Pd(CN)$_4$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23} [1]
Pd	0.0000(0)	0.0000(0)	0.0000(0)	0.0157(11)	0.0052(4)	0.0072(5)	−0.0003(1)	0.0086(7)	−0.0001(1)
Ni	0.0000(0)	0.0000(0)	0.5000(0)	0.0170(11)	0.0062(4)	0.0104(6)	0.0004(3)	0.0116(9)	0.0000(2)
C(1)	0.9533(17)	0.0178(8)	0.1745(10)	0.0298(32)	0.0060(7)	0.0060(11)	−0.0122(20)	0.0191(32)	−0.0020(11)
N(1)	0.9488(22)	0.0226(10)	0.2861(13)	0.0533(47)	0.0091(8)	0.0169(17)	−0.0279(33)	0.0421(51)	−0.0126(18)
C(2)	0.2630(14)	0.9282(10)	0.1455(10)	0.0177(22)	0.0101(10)	0.0089(11)	0.0013(22)	0.0078(27)	−0.0021(15)
N(2)	0.4223(17)	0.8923(11)	0.2234(12)	0.0283(29)	0.0133(13)	0.0180(17)	0.0095(29)	0.0094(37)	−0.0023(22)
C(3)	0.9573(21)	0.2584(14)	0.5694(21)	0.0290(36)	0.0119(15)	0.0302(30)	0.0063(35)	0.0188(56)	−0.0128(34)
C(4)	0.2538(21)	0.7822(13)	0.5166(18)	0.0322(39)	0.0098(13)	0.0259(26)	0.0042(32)	0.0042(32)	0.0009(26)
N(3)	0.1144(13)	0.1827(8)	0.5454(10)	0.0205(21)	0.0073(8)	0.0141(12)	0.0012(18)	0.0100(27)	−0.0004(14)
N(4)	0.2756(13)	0.9179(9)	0.5152(10)	0.0221(22)	0.0094(9)	0.0144(13)	0.0029(20)	0.0188(29)	0.0021(16)

[1] The form of the thermal ellipsoid is: exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell)]$. Numbers in parantheses here and in succeeding tables are the estimated standard deviations in the least significant digits.

Table 4. *Root-mean-square amplitudes of vibration* (Å)

Atom	Max.	Intermed.	Min.
Pd	0.185	0.176	0.174
Ni	0.211	0.191	0.187
C(1)	0.274	0.160	0.113
N(1)	0.382	0.207	0.159
C(2)	0.249	0.205	0.186
N(2)	0.330	0.267	0.223
C(3)	0.399	0.262	0.209
C(4)	0.346	0.269	0.231
N(3)	0.260	0.212	0.202
N(4)	0.255	0.228	0.202

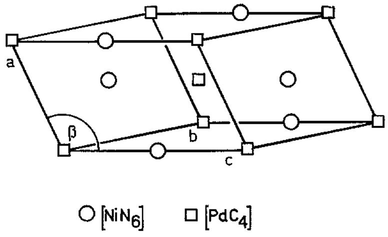

Fig. 2

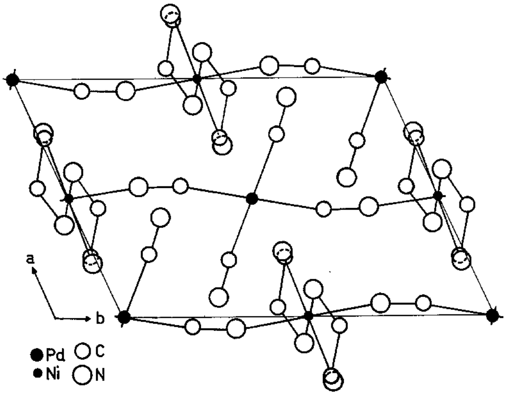

Fig. 3

Fig. 2. Packing diagram for $Ni(en)_2Pd(CN)_4$

Fig. 3. Projection of the unit cell of $Ni(en)_2Pd(CN)_4$ along the *b*-axis

N–H stretching frequencies (3321, 3317, 3302, 3280 cm^{-1}) are consistent with weak hydrogen bonds [11].

Because the nickel is located at a center of symmetry, the two chelate rings of the trans-$Ni(en)_2(NC)_2$ complex belong to the "gauche" ($\delta\lambda$)-conformation. The two carbon atoms are approximately +0.45 Å and −0.07 Å outside the Ni–N(3)–N(4) plane of the chelate ring. Also, a similar arrangement has been found in the structure of trans-$Co(en)_2Cl_2$ [12].

Table 5. *Interatomic distances and angles (Å, Deg.) of* $Ni(en)_2Pd(CN)_4$

Bond		Angle	
Pd–Ni	5.065(5)	C(1)–PdC(2)	80.7(4)
Pd–C(1)	1.943(8)	C(2)–Pd–C(2)	180.0(0)
Pd–C(2)	1.994(8)	C(1)–Pd–C(1)	180.0(0)
C(1)–N(1)	1.146(14)	N(1)–Ni–N(3)	90.0(2)
C(2)–N(2)	1.147(12)	N(1)–Ni–N(4)	82.6(5)
Ni–N(1)	2.054(11)	N(3)–Ni–N(4)	96.1(4)
Ni–N(3)	2.101(8)	N(1)–C(1)–Pd	171.9(6)
Ni–N(4)	2.110(6)	N(2)–C(2)–Pd	174.3(6)
C(3)–N(3)	1.490(11)	C(4)–C(3)–N(3)	113.9(8)
C(3)–C(4)	1.458(16)	C(3)–C(4)–N(4)	112.2(8)
C(4)–N(4)	1.466(16)	Ni–N(3)–C(3)	107.0(6)
		Ni–N(4)–C(4)	108.4(9)

Important bond distances and angles together with their estimated standard deviations are listed in Table 5. The distances Pd–C and Ni–N within the chain are about 0.05 Å shorter than the corresponding distances outside the chain. No such difference is observed in the bond length of the bridged and terminal cyanide. An unusually short distance is found between the two carbon atoms of the ethylenediamine ring. Also, other ethylenediamine metal complexes exhibit a

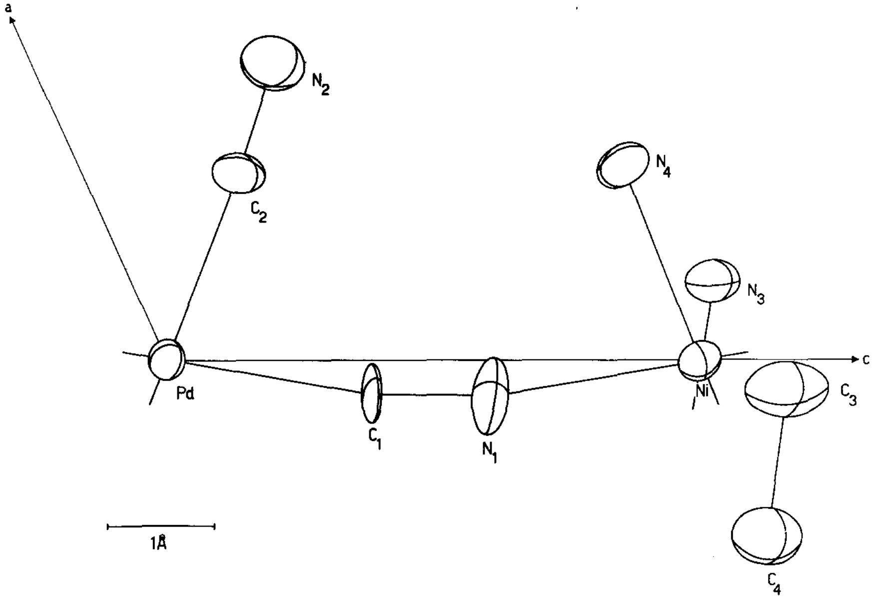

Fig. 4. Projection of the principal vibration axes on the (010)-plane

contraction of the C–C bond compared with the aliphatic distance of 1.54 Å [14]. We believe that the bond length of only 1.46 Å has been affected by systematic errors in the data. The C–N-distances in the ethylenediamine molecule agree with the usual value of 1.48 Å [13]. The coordination polyhedron of $[NiN_6]$ as well as that of $[PdC_4]$, differs slightly from ideal octahedral and square planar geometry.

A projection on the (010)-plane of the principal axes of the temperature ellipsoids is shown in Fig. 4. The longest axes of vibration are approximately perpendicular to the bond directions. The thermal ellipsoids of the carbon and nitrogen atoms of the bridged cyanide ions are as expected smaller than those of the same atoms in the terminal groups.

5. Experimental

Violet crystals of $Ni(en)_2Pd(CN)_4$ were grown by slow interdiffusion of aqueous solutions of $K_2Pd(CN)_4 \cdot H_2O$ and $NiSO_4 \cdot 6H_2O$/ethylenediamine. The mole ratio was Ni:Pd:en = 1:1:2.1. The pseudo-hexagonal prismatic crystals were analyzed for C, H, and N:

Calculated for $Ni(C_2H_8N_2)_2Pd(CN)_4$: C 24.7%, H 4.1%, N 28.8%.
Found : C 24.7%, H 4.1%, N 28.6%.

The density was measured pycnometrically (*n*-hexane, decahydronaphthalene). Infrared spectra were measured with a Beckman IR-9 (KBr-discs), reflectance spectra (5–50 kK) with a Zeiss PMQ II-RA2-RA3.

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