Butyl, isobutyl, and hexyl cyanate have been prepared earlier [1,10] and were identified by comparison of their infrared spectra with authentic materials.

Nonyl and undecyl cyanate are non-lachrymatory, pleasantly smelling liquids, in contrast to the lower members.

1. Jensen, K. A., Due, M. and Holm, A. *Acta Chem. Scand.* **19** (1965) 438.
2. Holm, A. *Acta Chem. Scand. To be published.*
3. Jensen, K. A., Due, M., Holm, A. and Wentrup, C. *Acta Chem. Scand.* **20** (1966) 2091.
4. Groving, N. and Holm, A. *Acta Chem. Scand.* **19** (1965) 443.
5. Zinner, G. and Weber, R. O. *Pharmazie* **21** (1966) 23.
6. Jensen, K. A., Anthoni, U. and Holm, A. *Acta Chem. Scand. In press.*
7. Béhal, A. *Bull. Soc. Chim. France* **25** (1919) 480.
8. Thiele, J. and Dent, F. *Ann.* **302** (1898) 271.
9. Schmidt, O. *Z. physik. Chem. (Leipzig)* **58** (1907) 514.
10. Jensen, K. A., Holm, A., Wentrup, C. and Møller, J. *Acta Chem. Scand.* **20** (1966) 2107.

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Note on $[Ni(en)_2][AgX_2]_2$ ($X = Br$ and I)

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It has been observed that in some cases small differences in chemical structure are responsible for a change in configuration. Thus, the nickel(II) salicylaldoxime complex is yellow and diamagnetic in benzene solution and in the solid state, and has been shown to be planar by X-ray analysis,[1] but its solution in pyridine is blue and paramagnetic. Similarly, two series of bis(ethylenediamine)nickel(II) complexes are known.[2] One, exemplified by the salt $[Ni(en)_2][AgBr_2]_2$, consists of orange and diamagnetic compounds, the other, exemplified by $[Ni(en)_2]SO_4$, of blue and paramagnetic ones. Sone and Kato [3] have observed that the blue-violet colour of an alcoholic solution of $[Ni(en)_2(H_2O)_2]^{2+}$ becomes yellowish with rise in temperature and the same type of thermochromism was also found in its aqueous solution containing $NaClO_4$. They claim, from spectrophotometric studies, that there exists a dehydration equilibrium of the complex ion, in which the yellow planar complex $[Ni(en)_2]^{2+}$ is produced in the solution from the octahedral $[Ni(en)_2(H_2O)_2]^{2+}$ complex. Brown and Lingafelter [4] have determined the crystal structure of the blue-violet $[Ni(en)_2(NCS)_2]$ and have found a nearly regular octahedral configuration contrary to the tetrahedral arrangement proposed by Pauling.[5] In the present work attention has been focused upon the orange coloured type of $[Ni(en)_2]^{2+}$ complexes. This note reports on the preparation and crystal data for $[Ni(en)_2][AgBr_2]_2$ and $[Ni(en)_2][AgI_2]_2$.

Preparation and analysis. The method used by Harris [6] in his preparation of $[Ni(en)_2][AgIBr]_2$ has been modified for the preparation of $[Ni(en)_2][AgBr_2]_2$ and $[Ni(en)_2][AgI_2]_2$ in order to avoid the inconvenience of coprecipitation of NH_4Br and NH_4I, respectively.

$[Ni(en)_2][AgBr_2]_2$: To a hot solution of 60 g NH_4Br and 1.88 g AgBr. (0.01 mole) in 100 ml water was added a hot solution of 2.15 g $[Ni(en)_2(H_2O)_2]Br_2$ and 5 g NH_4Br in 12.5 ml. On cooling, beautiful, well-developed, orange crystals of $[Ni(en)_2][AgBr_2]_2$ separated out. These were dried between filter papers and washed with alcohol and acetone (Yield: 1.4 g).

Nickel was determined as nickel dimethylglyoxime, ethylenediamine by the Kjeldahl method, silver as silver bromide and bromide as silver bromide. (Found: Ni 8.28; Ag 29.96; Br 44.80; en 16.83. Calc. for $[Ni(en)_2][AgBr_2]_2$: Ni 8.22; Ag 30.20; Br 44.75; en 16.83).

$[Ni(en)_2][AgI_2]_2$ was prepared and analyzed in a similar way.

Unit cell dimensions were calculated by a least-squares procedure on the observed $\sin^2\theta$ values, obtained from Guinier photographs taken with Cu$K\alpha$ radiation. Single crystal data have been collected by the Weissenberg method for $[Ni(en)_2][AgBr_2]_2$ and by a single-crystal automatic diffractometer (PAILRED) for $[Ni(en)_2][AgI_2]_2$.

Table 1. Powder diffraction data for $[Ni(en)_2][AgBr_2]_2$ taken in a Guinier camera with Cu$K\alpha$ radiation using $Pb(NO_3)_2$ (a=7.8566 Å) as an internal standard. λ(Cu$K\alpha_1$)=1.54051 Å.

h k l	$\sin^2\theta_{obs}$ $\times 10^5$	$\sin^2\theta_{calc}$ $\times 10^5$	I_{obs}	d_{obs}
1 1 0	1124	1125	vst	7.265
0 2 0	1457	1453	vst	6.381
0 0 1	1840	1833		5.678
2 0 0	3049	3045	m	4.411
0 2 1	3281	3286	m	4.252
2 2 $\bar{1}$	3946	3963	vvw	3.878
1 3 0	4025	4031	vvw	3.839
1 1 1	4139	4141	st	3.786
1 3 $\bar{1}$	4678	4679	vst	3.561
3 1 $\bar{1}$	5489	5495	vst	3.288
2 0 $\bar{2}$	5629	5640	w	3.247
0 4 0	5804	5812	m	3.197
1 1 $\bar{2}$	6082	6087	vw	3.123
2 2 $\bar{2}$	7119	7093	st	2.887
3 1 0	7203	7215	st	2.870
0 0 2	7327	7331	w	2.846
3 1 $\bar{2}$	7448	7441	st	2.822
0 4 1	7646	7645	st	2.786
2 2 1	8695	8699	vvw	2.612
0 2 2	8783	8784	st	2.599
1 3 $\bar{2}$	8994	8993	m	2.568
1 5 0	9845	9843	vw	2.455
3 3 $\bar{2}$	10355	10347	m+	2.394
4 2 $\bar{1}$	10735	10730	vw	2.351
1 1 2	10813	10824	w	2.342
4 2 $\bar{2}$	11487	11492	st	2.273
4 0 0	12166	12181	m	2.208
3 1 1	12570	12600	vvw	2.173
1 5 1	12853	12859	vw	2.148
3 1 $\bar{3}$	13093	13053	m	2.129
2 4 1		13058		
0 6 0		13077		
0 4 2	13144	13143	w	2.125
4 2 0	13630	13634	m	2.086
1 3 2	13720	13730	st	2.079
1 1 $\bar{3}$	14062	14067	m−	2.054
3 5 $\bar{1}$	14232	14213	m+	2.042
4 0 $\bar{3}$	14456	14466	vvw	2.026
1 5 $\bar{2}$	14765	14805	vvw	2.005
4 4 1	15096	15089	vvw	1.9825
2 0 2		15113		
3 3 1	15497	15506	vw	1.9566
4 4 $\bar{2}$	15865	15851	w	1.9338
2 6 0	16141	16122	m	1.9172
3 5 2		16159		
0 0 3	16497	16495	vw	1.8964
5 3 $\bar{2}$	17789	17792	vw	1.8262
0 2 3	17962	17948	vvw	1.8174
5 1 $\bar{3}$	18102	18129	vw	1.8104
1 7 0	18538	18561	vw	1.7890
1 5 2	19525	19542	vw	1.7432
4 2 1	20205	20203	w	1.7136
3 1 $\bar{4}$	22319	22329	m	1.6304
4 0 $\bar{4}$	22544	22559	w	1.6223

Table 2. Powder diffraction data for $[Ni(en)_2][AgI_2]_2$ taken in a Guinier camera with Cu$K\alpha$ radiation using $Pb(NO_3)_2$ (a=7.8566 Å) as an internal standard. λ(Cu$K\alpha_1$)=1.54051 Å.

h k l	$\sin^2\theta_{obs}$ $\times 10^5$	$\sin^2\theta_{calc}$ $\times 10^5$	I_{obs}	d_{obs}
0 1 1	1044	1042	vst	7.540
0 2 0	1386	1388	vst	6.543
1 0 1	2268	2283	vw	5.115
0 0 2	2777	2779	w	4.622
$\bar{1}$ 2 1	3062	3069	w	4.402
$\bar{1}$ 1 2	3802	3812	st	3.951
0 2 2	4169	4168	vvw	3.733
1 3 0	4410	4411	vst	3.668
1 1 2	5006	5016	st	3.443
2 0 0	5130	5149	w	3.401
0 4 0	5552	5553	vw	3.269
0 1 3	6582	6601	m	3.002
2 1 1	6769	6793	m	2.961
$\bar{1}$ 4 1	7232	7234	vw	2.864
$\bar{2}$ 2 2	8098	8112	m	2.707
$\bar{2}$ 3 1	8339	8365	vw	2.677
0 5 1	9351	9371	vvw	2.519
2 3 1	9571	9569	st	2.490
1 2 3	9793	9833	vvw	2.461
$\bar{2}$ 1 3	9943	9943	vvw	2.443
2 2 2	10531	10521	w	2.374
$\bar{2}$ 4 0	10708	10701	m	2.354
$\bar{1}$ 5 2	12121	12140	vvw	2.212
$\bar{1}$ 4 3	12244	12190	vvw	2.201
$\bar{2}$ 4 2		12278		
$\bar{2}$ 3 3	12724	12720	w	2.159
$\bar{3}$ 1 2	12870	12905	vw	2.147
3 0 1	13165	13184	vvw	2.123
1 5 2	13335	13345	vvw	2.109
$\bar{2}$ 0 4	13958	13858	vw	2.062
1 4 3		13997		
$\bar{1}$ 3 4	14307	14324	vvw	2.036
2 4 2	14703	14686	vw	2.009
2 5 1	15109	15122	vvw	1.9816
$\bar{3}$ 0 3		15129		
3 1 2	16478	16519	vvw	1.8975
0 4 4	16711	16671	vvw	1.8834
1 3 4		16733		
0 7 1	17732	17700	vvw	1.8292
0 1 5		17719		
$\bar{4}$ 1 1	20416	20434	w	1.7047
$\bar{1}$ 7 2		20469		
4 0 0	20623	20596	vvw	1.6961
$\bar{4}$ 0 2	20979	20967	vvw	1.6817
1 7 2	21645	21674	vvw	1.6556
3 2 3	21904	21937	vvw	1.6458
0 8 0	22246	22210	vvw	1.6311
$\bar{3}$ 3 4		22213		
0 6 4	23647	23611	vvw	1.5840
$\bar{1}$ 1 6	24854	24843	vvw	1.5450
3 5 2		24847		
$\bar{3}$ 6 3	27584	27622	vvw	1.4666
$\bar{2}$ 2 6	27926	27940	vvw	1.4576
2 3 5	28659	28565	vvw	1.4388

Table 1. Continued.

4 2 $\bar{4}$ 6 2 $\bar{3}$	24047	24012 24040	vw	1.5744
3 3 2 4 4 1	24541	24556 24562	w	1.5548
4 6 0	25266	25258	w	1.5324

Both compounds are monoclinic with the cell dimensions

$[Ni(en)_2][AgBr_2]_2$: $a = 10.202 \pm 0.006$ Å, $b = 12.780 \pm 0.008$ Å, $c = 6.575 \pm 0.008$ Å, $\beta = 120.08 \pm 0.04°$, $V = 741.8$ Å^3. $[Ni(en)_2][AgI_2]_2$: $a = 10.696 \pm 0.010$ Å, $b = 13.075 \pm 0.017$ Å, $c = 6.877 \pm 0.007$ Å, $\beta = 120.24 \pm 0.07°$, $V = 830.0$ Å^3. (The errors given are 3σ). The axial ratio $a:b:c$ is thus 1.552:1.944:1.000 for $[Ni(en)_2][AgBr_2]_2$ and 1.555:1.901:1.000 for $[Ni(en)_2][AgI_2]_2$. Systematic absences have been observed for planes of the type hkl with $h+k=2n+1$ for both compounds. The above evidence, together with the observation that the Patterson functions are very similar, strongly supports isomorphism. Possible space groups are $C2$ (No. 5), Cm (No. 8), and $C2/m$ (No. 12). Although the intensity distribution test for $hk0$ reflexions for $[Ni(en)_2][AgBr_2]_2$ shows the distribution expected for a centrosymmetric crystal this does not prove that the space group is $C2/m$.

The density of $[Ni(en)_2][AgBr_2]_2$, as determined by weighing a sample in air and in benzene, is 3.06. The density for a unit cell containing two formula units is 3.197 g/cm^3.

Observed and calculated $\sin^2\theta$ values are listed in Table 1 and 2. For $[Ni(en)_2][AgI_2]_2$ the indexing refers to a reduced cell (I-centered, transformation matrix $\{101/010/\bar{1}00\}$) with $a = 6.877$ Å, $b = 13.075$ Å, $c = 9.359$ Å, and $\beta = 99.16°$.

The structure work is in progress and a full report will be published in a forthcoming paper.

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1. Cox, E. G., Pinkard, F. W., Wardlaw, W. and Webster, K. C. *J. Chem. Soc.* **1935** 459.
2. Nyholm, R. S. *Chem. Rev.* **53** (1953) 278.
3. Sone, K. and Kato, M. *Z. anorg. allgem. Chem.* **301** (1959) 277.
4. Brown, B. W. and Lingafelter, E. C. *Acta Cryst.* **16** (1963) 753.
5. Pauling, L. *The Nature of the Chemical Bond*, 3rd. Ed., Ithaca, Cornell Univ. Press, Ithaca, p. 168.
6. Harris, C. M. *J. Proc. Roy. Soc. N. S. Wales* **85** (4) (1951) 142.

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Studies on Peroxidomolybdates

III. Unit Cell Dimensions for Two Peroxidoheptamolybdates

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It has been found by Stomberg and Trysberg [1] that two peroxidomolybdates can be obtained from potassium molybdate solutions containing hydrogen peroxide, with an H_2O_2:Mo ratio equal to 0.1 – 0.8 in the pH range 5.8 – 6.8. The empirical formulae of these two compounds are:

1. $K_6Mo_7O_{22}(O_2)_2 \cdot 9H_2O$ (o-rh.)
2. $K_6Mo_7O_{24-x}(O_2)_x \cdot 9H_2O$ (mon.) $(0.5 < x < 3)$

The exact limits for x have not yet been settled.

The above formulae are consistent with the replacement of an oxygen ion in the molybdenum complex by a peroxide group. It is, however, impossible to say at the present stage of the investigation whether or not this is so. The peroxide could equally well partly or completely be hydrogen peroxide of crystallization. For compound 2 there is even a slight indication (see 2 below) that the latter possibility is the most probable one.

The unit cell dimensions and the conditions limiting possible reflexions were determined for the two crystalline materials by rotation, Weissenberg, and powder diffraction methods. Accurate unit cell parameters were obtained from measured