

## 2-Chloro-juglone:

Yellow-brown, flat prisms from ethyl alcohol solution.

<i>a</i>	7.17 Å	$\rho_0$	1.55
<i>b</i>	7.79 Å	$\rho_x$	1.58
<i>c</i>	8.02 Å		
$\alpha$	100.0°	<i>Z</i>	2
$\beta$	101.4°	Space group	$\bar{1}$
$\gamma$	88.7°		

## 2,3,8-Tribromo-juglone:

<i>a</i>	18.21 Å	$\rho_0$	2.475
<i>b</i>	4.75 Å	$\rho_x$	2.465
<i>c</i>	25.58 Å	<i>Z</i>	8
		Space group	<i>Pna2</i> <sub>1</sub>

## 1,4-Dihydroxy-anthraquinone I:

Red-orange leaves from ethyl alcohol solution.

<i>a</i>	10.40 Å	$\rho_0$	1.52
<i>b</i>	6.04 Å	$\rho_x$	1.53
<i>c</i>	16.65 Å	<i>Z</i>	4
$\beta$	95.2°	Space group	<i>P2</i> <sub>1</sub> / <i>n</i>

## 1,4-Dihydroxy-anthraquinone II:

Dark red crystals formed by slow cooling of the melt. Some crystals revert to modification I at room temperature.

<i>a</i>	3.77 Å	$\rho_0$	1.50
<i>b</i>	9.49 Å	$\rho_x$	1.51
<i>c</i>	14.80 Å	<i>Z</i>	2
$\beta$	93.0°	Space group	<i>Pc</i>

## 1,5-Dihydroxy-anthraquinone:

Yellow needles from acetic acid solution.

<i>a</i>	6.02 Å	$\rho_0$	1.56
<i>b</i>	5.30 Å	$\rho_x$	1.60
<i>c</i>	15.70 Å	<i>Z</i>	2
$\beta$	94.0°	Space group	<i>P2</i> <sub>1</sub> / <i>c</i>
		Molecular symmetry	$\bar{1}$

## 1,4,5,8-Tetrahydroxy-2,3,6,7-dibenzanthraquinone:

Dark red prisms of metallic lustre from hot nitrobenzene solution.

<i>a</i>	17.52 Å	$\rho_0$	1.51
<i>b</i>	3.83 Å	$\rho_x$	1.54
<i>c</i>	23.9 Å	<i>Z</i>	4
$\beta$	90.0°	Space group	<i>P2</i> <sub>1</sub> / <i>c</i>

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## The Crystal Structure of Potassium Nickel (IV) Hexaoxidioiodate(VII)

LOWELL P. EDDY and  
NILS-GÖSTA VANNERBERG

Department of Chemistry, Western  
Washington State College, Washington, USA  
Department of Inorganic Chemistry,  
Chalmers Institute of Technology and  
University of Gothenburg, Gothenburg,  
Sweden

A tentative structure of  $\text{KNiIO}_6$  has previously been published in this journal by Vannerberg and Blockhammar.<sup>1</sup> Eddy has reached the same result independently, also from powder data, but using a considerably larger number of reflexions. It was thus thought worthwhile to try to refine the structure by least squares methods.

In those cases where there was considerable overlap between two or more reflexions, the measured intensities were distributed according to the previously calculated intensities. The structure was

Table 1. Atomic and thermal parameters for  $\text{KNiIO}_6$ .

Atom	X	Y	Z	B
K	0	0	0	4.4
Ni	1/3	2/3	1/2	3.2
I	2/3	1/3	1/2	1.2
O <sub>1</sub>	0.671	0.039	0.312	1.7
O <sub>2</sub>	0.961	0.329	0.688	1.7
O <sub>3</sub>	0.961	0.631	0.312	1.7
O <sub>4</sub>	0.671	0.631	0.688	1.7
O <sub>5</sub>	0.369	0.329	0.312	1.7
O <sub>6</sub>	0.369	0.039	0.688	1.7

regarded as being triclinic with space-group *P1*. The least squares refinement was based on the observed structure factors, and convergence was obtained after only four cycles. The oxygen atomic parameters did not deviate much from those expected for hexagonal symmetry. Both space-groups *P3*, No. 143 and *P312*, No. 149 were, however, possible. The former gave an *R* factor of 0.108 while the latter gave an *R* factor of 0.120. In spite of this, the space-group *P312* must be considered to be most probable since it gives a coordination

Table 2. Bond distances and angles in KNiIO<sub>6</sub>.

K — O	2.56 Å
Ni — O	2.10 Å
I — O	1.85 Å
O <sub>1</sub> — K — O <sub>2</sub>	103°
— O <sub>3</sub>	72
— O <sub>4</sub>	113
— O <sub>5</sub>	72
— O <sub>6</sub>	172
O <sub>1</sub> — Ni — O <sub>2</sub>	172
— O <sub>3</sub>	94
— O <sub>4</sub>	93
— O <sub>5</sub>	94
— O <sub>6</sub>	80
O <sub>1</sub> — I — O <sub>2</sub>	93
— O <sub>3</sub>	87
— O <sub>4</sub>	179
— O <sub>5</sub>	87
— O <sub>6</sub>	94

around the iodine atom which is octahedral within the limits of error. Moreover, the I—O distance is found to be 1.85 Å in agreement with the value found in the compounds Ag<sub>2</sub>H<sub>3</sub>IO<sub>6</sub><sup>2</sup> and K<sub>4</sub>H<sub>2</sub>I<sub>2</sub>O<sub>10</sub>.<sup>3</sup> The space-group *P*3 places three oxygen atoms near the iodine atom (1.72 Å) and three further away (2.05 Å). There are no reasons to believe that the hexaoxidoiodate (VII) ion should depart from the usual octahedral symmetry. The corresponding xenate ion is octahedral.<sup>3</sup>

The least squares refinement gives the previously published tentative structure further support. It has also been possible to distinguish between the I—O and the Ni—O distances. The first is calculated to be 1.85 Å and the second 2.10 Å.

The standard deviations obtained from the least squares refinement are far too

Table 3.

<i>hkl</i>	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>
100	43	56	28.0	34.4	400	3	1	34.3	24.9
101					401	5	3	31.4	25.2
002	24	21	51.5	53.6	304	2	4	20.2	32.0
110	57	47	58.8	57.9	{313			16.4	19.5
{111	43	54	19.9	20.0	{31 $\bar{3}$	3	4	18.4	20.9
{ $\bar{1}\bar{1}\bar{1}$			52.8	64.7	006	1	1	35.1	37.2
200	7	4	24.9	20.0	320	1	1	14.1	14.5
201	28	27	37.0	39.4	{321			28.5	23.3
{112	63	79	50.7	55.5	{32 $\bar{1}$	6	3	19.6	17.1
{ $\bar{1}\bar{1}\bar{2}$			66.0	84.5	{215			20.6	21.5
103	17	17	33.0	35.6	{21 $\bar{5}$	4	4	18.9	19.1
202	8	9	23.8	27.3	{224			25.8	23.4
210	7	5	24.2	21.3	{2 $\bar{2}\bar{4}$	5	4	35.3	34.3
{211	36	22	31.8	28.9	{322			23.6	21.3
{21 $\bar{1}$			47.9	38.8	{32 $\bar{2}$	5	3	19.6	16.6
004	4	4	49.2	50.4	{411			17.1	17.5
203	10	10	32.8	35.5	{41 $\bar{1}$	5	4	25.3	26.0
300	25	30	75.3	62.7	{412			24.0	24.1
301	13	11	39.6	40.2	{41 $\bar{2}$	8	8	28.0	30.2
{114	13	13	51.0	54.6	{323			15.2	19.9
{ $\bar{1}\bar{1}\bar{4}$			31.0	31.0	{32 $\bar{3}$	4	5	18.2	22.2
{213			24.1	30.9	{225			16.0	15.8
{21 $\bar{3}$	6	9	18.2	27.9	{22 $\bar{5}$	2	2	19.9	19.2
220	4	3	37.0	35.4	{413			20.0	22.7
{221	5	4	35.1	36.7	{41 $\bar{3}$	5	6	17.0	19.9
{ $\bar{2}\bar{2}\bar{1}$			20.4	21.0	502	4	2	21.4	16.2
310	3	3	22.7	24.1	331	3	4	18.7	20.6
{311	12	6	35.3	29.3	33 $\bar{1}$			16.8	19.3
{31 $\bar{1}$			29.4	25.8	420	1	2	10.0	14.0
{222	10	8	45.7	46.1	421	3	6	9.5	13.8
{22 $\bar{2}$			39.0	35.3	42 $\bar{1}$			12.8	18.8
{214	4	3	22.3	22.9					
{ $\bar{2}\bar{1}\bar{4}$			15.8	15.4					

small to be of any real value, and are estimated to be about 0.06 Å. The corresponding value for the angles is then 3°.

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## Radiation-induced Organic Sulfur Radicals at 77°K

THORMOD HENRIKSEN and  
TORE SANNER

*Norsk Hydro's Institute for Cancer Research,  
The Norwegian Radium Hospital, Montebello,  
Norway*

The electron spin resonance (ESR) spectra induced when organic substances containing SH or SS groups are irradiated at room temperature or at low temperatures followed by annealing at 200°K or higher, are in part due to the formation of the organo-sulfur radical,  $R-CX_2-S^{\cdot}$ .<sup>1-5</sup> In polycrystalline samples these sulfur radicals exhibit a resonance similar to that shown in Fig. 1 (upper curve).

Studies of irradiated molecular mixtures have yielded support for the hypothesis that the above sulfur radicals may be formed by intermolecular radical reac-

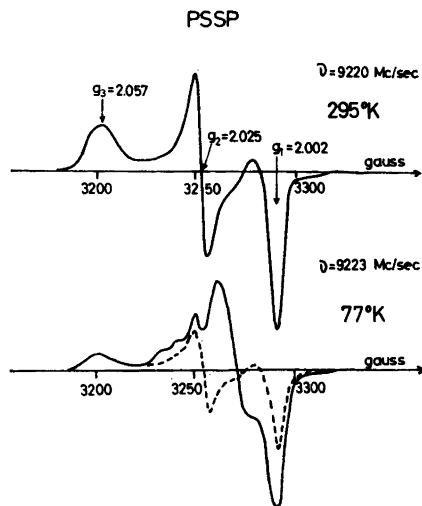


Fig. 1. First derivative ESR spectra of oxidized penicillamine irradiated at 295°K (upper curve) and at 77°K. PSSP was prepared by oxidation of PSH (Sigma Chem. Co.) with oxygen. The samples were freeze-dried from a solution of pH = 8.4 and irradiated in vacuum with 220 kV X-rays to a dose of 0.5 megarad. The spectra were recorded at 77°K with an X-band spectrometer. The dashed curve, which is the sulfur pattern, is identical with the upper spectrum. With the application of Kneubühl's<sup>9</sup> theory the three principal  $g$ -values can be calculated. The results given in this figure are in excellent agreement with those for other organo-sulfur radicals of the type  $R-CX_2-S$ .

tions.<sup>6</sup> Thus, in experiments where molecular mixtures containing a thiol or a disulfide and a macromolecule have been irradiated, at low temperatures and subsequently heat-treated, a transfer of radiation energy from the macromolecule to the sulfur-component with the formation of  $R-CX_2-S$  radicals has been observed. On the other hand, Akasaka *et al.*<sup>7</sup> have recently suggested that the organo-sulfur radicals may be formed by an intramolecular transformation. From experiments on single crystals of cystine dihydrochloride, irradiated at 77°K, both Akasaka *et al.*<sup>7</sup> and Box and Freund<sup>8</sup> suggest that one of the radicals initially formed is a charged radical with an unpaired electron in the S-S bond,  $(R-\dot{C}H_2-S-S-\dot{C}H_2-R)^{\cdot}$ . Subsequent heat-treatment resulted in spectral changes and Akasaka *et al.*<sup>7</sup>