

**The Crystal Structure of two Modifications of Oxidodiperoxido-2,2'-dipyridylchromium(VI),**  
**[CrO(O<sub>2</sub>)<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)]**

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The crystals of the blue compound CrO<sub>2</sub>-dipy have been shown by three-dimensional X-ray analysis and least-squares refinement to be built up of oxidodiperoxido-2,2'-dipyridylchromium(VI) molecules held together by van der Waals' forces. Two different crystalline modifications of the compound have been subjected to structural investigation. One is orthorhombic and belongs to space group *Pnma*, with four molecules in a unit cell of the dimensions  $a=11.535$  Å,  $b=6.869$  Å,  $c=13.784$  Å, and  $V=1092.2$  Å<sup>3</sup>. The other is triclinic, space group *P1̄*, with two molecules in a unit cell of the dimensions  $a=9.212$  Å,  $b=8.773$  Å,  $c=7.060$  Å,  $\alpha=94.18^\circ$ ,  $\beta=92.13^\circ$ ,  $\gamma=108.78^\circ$ , and  $V=537.6$  Å<sup>3</sup>.

Chromium is coordinated, in both modifications, to seven atoms in the form of a pentagonal bipyramid, the equatorial plane of which is formed from the four peroxidic oxygen atoms and one nitrogen atom, the second nitrogen atom and the oxide oxygen atom being situated at the apices. The chromium atom is displaced 0.31 Å from the equatorial plane towards the oxygen atom.

Average bond distances are: Cr—O<sub>peroxido</sub> 1.85 Å, Cr—O<sub>oxido</sub> 1.57 Å, Cr—N<sub>equatorial</sub> 2.11 Å, Cr—N<sub>apical</sub> 2.23 Å, O—O 1.40 Å, N—C 1.36 Å and C—C 1.41 Å.

In connection with his work on peroxochromates<sup>1</sup> Stomberg has shown that both mono- and bidentate ligands can coordinate to chromium in the so-called "peroxochromic acid", CrO(O<sub>2</sub>)<sub>2</sub>. This is exemplified by [CrO(O<sub>2</sub>)py]<sup>2\*</sup> and [CrO(O<sub>2</sub>)<sub>2</sub>ophen],<sup>3</sup> where chromium is six- and seven-coordinated, respectively. In the latter compound it was found that one Cr—N distance, 2.26 Å, was significantly longer than the other, 2.11 Å, and also longer than Cr—N distances observed in other compounds. This indicates that one nitrogen atom

\* The usual abbreviations have been used for the following ligands, *i.e.*: py=pyridine; dipy=2,2'-dipyridyl, ophen=1,10-phenanthroline (=ortho-phenanthroline).

is more loosely bound to chromium than the other.  $[\text{CrO}(\text{O}_2)_2\text{py}]$  may thus be regarded as being an extreme case in which one coordinated atom is completely missing. Dipy, like ophen, normally acts as a bidentate ligand, but, unlike ophen, it has the additional possibility of free rotation of the two pyridine rings about the C—C bond leading to a *trans*-configuration of the two nitrogen atoms, as observed in the solid state.<sup>4</sup> In view of this property and since preliminary photographs of  $[\text{CrO}(\text{O}_2)_2\text{dipy}]$  indicated another unit cell (triclinic) than  $[\text{CrO}(\text{O}_2)_2\text{ophen}]$  (orthorhombic), the present investigation was undertaken in order to examine the configuration about chromium in  $[\text{CrO}(\text{O}_2)_2\text{dipy}]$ .

### EXPERIMENTAL

*Preparation of crystals.* A solution of 2,2'-dipyridyl in acetone was added, in the cold, to an ethereal solution of peroxochromic acid, prepared according to Wiede,<sup>5</sup> whereupon a light blue microcrystalline precipitate of  $[\text{CrO}(\text{O}_2)_2\text{dipy}]$  formed immediately. The substance was recrystallized from acetone by slow evaporation (one to two months) at  $-20^\circ\text{C}$ . The crystals crystallized in two different forms: one needle-shaped (later shown to be orthorhombic with the needle-axis parallel to the crystallographic *b*-axis) and the other plate-shaped (a triclinic modification, the rhombic plates consisting of four intergrown single crystals whose crystallographic *c*-axes were parallel to the longest rhomb diagonal).

*Chromium content.* The amount of chromium was determined gravimetrically as  $\text{Cr}_2\text{O}_3$ . (Found: Cr 18.14. Calc. for  $[\text{CrO}(\text{O}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)]$ : Cr 18.04).

*X-Ray methods.* Approximate cell dimensions were obtained from rotation and Weissenberg photographs and, for the triclinic form, from precession photographs. More accurate dimensions were then calculated by a least-squares procedure using the  $\sin^2\theta$  values obtained from X-ray powder photographs taken in a Guinier focusing camera with  $\text{CuK}\alpha$  radiation using lead nitrate ( $a=7.8566 \text{ \AA}$  at  $21^\circ\text{C}$ ) as an internal standard.

Multiple-film (5 films) equi-inclination single crystal Weissenberg photographs were taken with copper radiation and rotation about  $[010]$  (layer lines 0–5) and  $[100]$  (layer lines 0–1) for the orthorhombic modification, and about  $[001]$  (layer lines 0–2) and  $[100]$  (layer line 0) for the triclinic form. The exposure times ranged from 14–25 h. Due to the low stability of the compound new crystals had to be mounted for each layer line. Since it proved impossible to find triclinic crystals suitable for single crystal X-ray purposes, only comparatively few reflexions could be registered and these were rather diffuse. Nor were better photographs obtained by using a low-temperature camera. It has not therefore been possible to collect a complete set of diffraction data for the triclinic form but those data collected have sufficed for a crude structure determination.

The reflexion intensities were estimated visually by comparison with an intensity scale obtained by the rotating sector method, and were corrected using Lorentz and polarization factors. Absorption and extinction effects were not considered ( $\mu=92 \text{ cm}^{-1}$ ,  $\mu R < 0.4$ ). The  $|F_o|$  values were brought on to an absolute scale by comparison with the finally calculated structure factors.

*Computing methods.* The computational work, including the Lorentz and polarization correction, Fourier summations, structure factor least-squares refinement and calculation of interatomic distances and angles and molecular planes, was performed on the electronic computer SAAB D21 with the aid of a set of crystallographic programmes written by Abrahamsson, Aleby, Larsson and Selin.<sup>6–10</sup>

The atomic scattering factors used in the calculation of the structure factors were taken from Volume III of the *International Tables for X-ray Crystallography*, 1962.

### STRUCTURE DETERMINATION OF THE ORTHORHOMBIC MODIFICATION

*Unit cell and space group.*  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh.})$  is orthorhombic with the unit cell dimensions

$$\begin{aligned}
 a &= 11.535 \pm 0.004 \text{ \AA} \\
 b &= 6.869 \pm 0.001 \text{ \AA} \\
 c &= 13.784 \pm 0.004 \text{ \AA} \\
 V &= 1092.2 \text{ \AA}^3
 \end{aligned}$$

Calculated and observed  $\sin^2\theta$ -values are given in Table 1.

Table 1. Observed lines in the powder diagram (Guinier focusing camera) of  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh})$ .  $\lambda(\text{CuK}\alpha_1) = 1.54051 \text{ \AA}$ .

$hkl$	$10^4 \sin^2\theta_{\text{obs}}$	$10^4 \sin^2\theta_{\text{calc}}$	$d_{\text{obs}}$	$I_{\text{obs}}$
0 1 1	1580	1570	6.128	m
1 0 2	1697	1695	5.913	st
2 0 0	1788	1784	5.760	m
1 1 1	2017	2016	5.424	st
2 1 0	3038	3041	4.419	vw
2 1 1	3359	3353	4.203	st
0 1 3	4079	4068	3.814	w
2 1 2	4276	4290	3.725	vw
0 2 0	5033	5030	3.433	vst
3 0 2	5254	5262	3.360	w
1 0 4	5440	5442	3.302	m
0 2 2	6287	6279	3.072	vw
3 0 3	6832	6823	2.947	vw
4 0 0	7139	7134	2.883	vw
3 0 4	9008	9009	2.566	m
2 3 0	13106	13101	2.128	vw
0 4 0	20118	20120	1.7173	m
5 2 4	21179	21173	1.6737	vw

Systematic absences were observed for the following reflexions:

$$\begin{aligned}
 0kl; & \quad k+l = 2n+1 \\
 h k 0; & \quad h = 2n+1
 \end{aligned}$$

Possible space groups are thus  $Pn2_1a$  (No. 33) and  $Pnma$  (No. 62). As is shown below all atoms occupy positions in space group  $Pnma$ .

The density of the crystals, as determined by the flotation method, is  $1.745 \text{ g/cm}^3$ . This corresponds to an elementary cell containing four molecules ( $\rho_{\text{calc.}} = 1.752 \text{ g/cm}^3$ ).

Table 2. Required Cr—Cr vectors between equivalent chromium atoms according to space group  $Pnma$ .

Position	Vector	$u$	$v$	$w$	Relative weight
4a or 4b	1	0	$\frac{1}{2}$	0	4
	2	$\frac{1}{2}$	0	$\frac{1}{2}$	4
	3	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	4
4c	4	$\pm \left[ \begin{array}{c} 2x \\ \frac{1}{2} \end{array} \right]$	$\frac{1}{2}$	$\pm \left[ \begin{array}{c} 2z \\ \frac{1}{2} \end{array} \right]$	1
	5	$\pm \left[ \begin{array}{c} -2x \\ \frac{1}{2} \end{array} \right]$	$\frac{1}{2}$	$\pm \left[ \begin{array}{c} \frac{1}{2} \\ -2z \end{array} \right]$	2
	6	$\pm \left[ \begin{array}{c} \frac{1}{2} \\ \frac{1}{2} \end{array} \right]$	0	$\pm \left[ \begin{array}{c} \frac{1}{2} \\ -2z \end{array} \right]$	2

Table 3. Observed large Patterson peaks for  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh})$ .

Peak	$u$	$v$	$w$	Peak height (arbitrary-units)
A	$\frac{1}{2}$	0	0.1204	456
B	$\frac{1}{2}$	$\frac{1}{2}$	0.3795	385
C	0	$\frac{1}{2}$	$\frac{1}{2}$	1238
D	0	0.2872	0	422
E	0	0.2468	$\sim 0.03$	385
F	0.119	0	0.109	168

*Structure determination.* The four chromium atoms in the unit cell may occupy one of the four-fold positions of space group  $Pnma$ . The expected interatomic vectors are listed in Table 2 and the largest peaks observed in Patterson space in Table 3. Identification of a consistent set of expected and observed peaks ( $A \equiv 6$ ,  $B \equiv 4$ ,  $C \equiv 5$ ) indicates that the chromium atoms occupy the position

$$4c \text{ with } x \approx 0.25 \quad y = \frac{1}{4} \quad z = 0.1898$$

(final coordinates are  $(0.2518; \frac{1}{4}; 0.1893)$ ).

The peaks D and E were assumed to be Cr—O<sub>peroxido</sub> vectors as these peaks lie close together and the lengths of the vectors are 1.97 Å and 1.75 Å, respectively. The two peroxido groups are thus situated on each side of the crystallographic mirror plane and the peroxido oxygen atoms therefore occupy two 8-fold positions with approximate  $y$ -values 0.50 and 0.54. The 2,2'-dipyridyl molecule is planar in the solid state.<sup>4</sup> By taking into account the available equivalent positions in the space group, the cell dimensions, the number of molecules in the cell and a plausible configuration of the ligands, it seemed highly probable that all carbon and nitrogen atoms could be situated in the mirror planes at  $y = \frac{1}{4}$  and  $y = \frac{3}{4}$  and thus occupy the positions  $4c$ .

A Fourier summation of the observed structure factors with signs derived from the chromium positions would give an electron density function with false mirror planes at  $x = \frac{1}{4}$  and  $x = \frac{3}{4}$  since  $x_{\text{Cr}} \approx \frac{1}{4}$ . Reasonable values for the coordinates of the carbon and nitrogen atoms in the ring-system could, however, be calculated from a knowledge of the space available, the structure of the 2,2'-dipyridyl molecule and the chromium and peroxido oxygen positions. The fifth oxygen atom must occupy a fourfold position and approximate coordinates were derived from the peak F in Table 3, assumed to represent a Cr—O vector. Structure factors were calculated from these atomic parameters with an overall temperature coefficient  $B = 3.5 \text{ \AA}^2$ , a reliability index,  $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ , of 0.41 being obtained. Using the resulting signs of the  $F$ -values an electron density calculation based on the reflexions  $h0l-h4l$  was undertaken. This showed well-resolved peaks at reasonable positions. With these parameters inserted in a new structure factor calculation the  $R$ -value dropped to 0.34. As it seemed likely that a correct structure had been arrived at, refinement of the parameters was begun.

Table 4. Atomic coordinates (expressed as fractions of the cell edges) and isotropic thermal parameters with their standard deviations for  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh})$ .

The temperature factor =  $\exp[-B(\sin^2\theta/\lambda^2)]$ . Space group *Pnma*. Four molecules in the unit cell. All atoms occupy the fourfold position *4c* except  $\text{O}_1$  and  $\text{O}_2$  which occupy the position *8d*.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	<i>B</i> ( $\text{\AA}^2$ )	$\sigma(B)$ ( $\text{\AA}^2$ )
Cr	0.2518	$\frac{1}{4}$	0.1893	0.0004		0.0002	3.0	0.1
$\text{O}_1$	0.2354	0.5259	0.1695	0.0010	0.0019	0.0007	4.1	0.3
$\text{O}_2$	0.1524	0.4334	0.2270	0.0010	0.0022	0.0008	4.9	0.3
$\text{O}_3$	0.3451	$\frac{1}{4}$	0.2723	0.0015		0.0012	4.6	0.4
$\text{N}_1$	0.3793	$\frac{1}{4}$	0.0796	0.0014		0.0012	2.8	0.4
$\text{N}_2$	0.1586	$\frac{1}{4}$	0.0472	0.0015		0.0012	2.8	0.4
$\text{C}_1$	0.4946	$\frac{1}{4}$	0.1033	0.0020		0.0017	3.7	0.5
$\text{C}_2$	0.5794	$\frac{1}{4}$	0.0317	0.0026		0.0022	6.0	0.7
$\text{C}_3$	0.5523	$\frac{1}{4}$	0.9380	0.0023		0.0019	4.6	0.6
$\text{C}_4$	0.4294	$\frac{1}{4}$	0.9090	0.0024		0.0021	5.6	0.7
$\text{C}_5$	0.3465	$\frac{1}{4}$	0.9839	0.0020		0.0015	3.5	0.6
$\text{C}_6$	0.2181	$\frac{1}{4}$	0.9682	0.0019		0.0017	4.1	0.6
$\text{C}_7$	0.1704	$\frac{1}{4}$	0.8777	0.0021		0.0017	4.1	0.5
$\text{C}_8$	0.0456	$\frac{1}{4}$	0.8638	0.0022		0.0021	4.9	0.6
$\text{C}_9$	-0.0118	$\frac{1}{4}$	0.9486	0.0025		0.0022	5.6	0.7
$\text{C}_{10}$	0.0376	$\frac{1}{4}$	0.0422	0.0021		0.0020	4.3	0.6

Table 5. Final weight analysis for  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh})$ .

$\sin^2\theta$ -interval	Number of reflexions	$\overline{w\Delta^2}$ (normalized)
0.0-0.1	42	1.08
0.1-0.2	71	0.62
0.2-0.3	59	0.99
0.3-0.4	56	0.72
0.4-0.5	47	1.36
0.5-0.6	34	1.73
0.6-0.7	19	1.23
0.7-0.8	11	0.67
0.8-0.9	4	0.23
0.9-1.0	0	—
$F_o$ -interval	Number of reflexions	$\overline{w\Delta^2}$ (normalized)
0-5	0	—
5-10	5	0.64
10-20	134	1.01
20-30	85	0.98
30-50	86	1.12
50-100	30	0.84
100-200	3	0.07

*Structure refinement.* The structure was refined by the structure factor least-squares method using all reflexions and the programme mentioned above. For each reflexion the weight  $w$  was computed according to  $w=1/\{1+[(|F_o|-a)/b]^2\}$ . The refinement was considered complete when all parameter shifts were less than one fifteenth of the corresponding standard deviations. The final atomic parameters obtained after the last refinement cycle are listed in Table 4. The  $R$ -value was then 0.116. An analysis of the weighting scheme after the last cycle is given in Table 5. Observed and calculated structure factors are presented in Table 6 (the contributions from the

Table 6. Observed and calculated structure factors for  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh})$ .

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
0	0	2	25	-21	8	0	5	22	-29	6	1	9	23	-20	4	2	6	14	-10	4	3	9	25	-24
0	0	4	38	35	8	0	6	18	20	6	1	11	18	14	4	2	8	27	24	4	3	11	15	16
0	0	6	17	15	8	0	7	16	-10	7	1	3	36	-34	4	2	10	26	-21	5	3	3	67	-69
0	0	8	51	-58	8	0	8	24	-29	7	1	4	14	16	4	2	12	17	14	5	3	5	49	50
0	0	14	16	-17	8	0	10	15	17	7	1	5	33	29	5	2	1	30	-29	5	3	2	24	-20
0	0	16	12	7	9	0	2	36	-41	7	1	6	21	-23	5	2	2	14	16	6	3	0	46	39
1	0	1	17	-11	9	0	6	25	-29	7	1	7	24	-27	5	2	3	25	-28	6	3	1	47	-45
1	0	2	92	-103	10	0	0	36	-54	7	1	10	13	-14	5	2	4	45	-45	6	3	3	27	26
1	0	3	35	-32	10	0	2	18	26	7	1	11	20	22	5	2	6	39	43	6	3	5	15	16
1	0	4	119	115	11	0	3	19	5	8	1	0	13	-11	5	2	8	24	-23	6	3	7	27	-29
1	0	5	48	45	0	1	3	71	80	8	1	1	45	-46	5	2	12	17	13	6	3	9	15	15
1	0	6	71	-72	0	1	5	38	-33	8	1	4	15	14	6	2	0	15	12	7	3	1	13	-8
1	0	10	47	49	0	1	7	39	-34	8	1	7	13	-7	6	2	2	34	-34	7	3	2	14	-11
1	0	11	51	-51	0	1	9	48	45	8	1	9	21	27	6	2	4	14	12	7	3	3	38	36
1	0	12	18	-13	1	1	1	93	-109	9	1	1	20	-21	6	2	5	22	20	7	3	5	51	-30
1	0	14	14	12	1	1	2	24	25	9	1	2	20	19	6	2	8	22	-25	7	3	7	21	23
2	0	0	99	-102	1	1	5	48	-48	9	1	3	17	18	6	2	10	20	20	7	3	8	18	16
2	0	1	25	-18	1	1	6	37	-37	9	1	4	16	16	7	2	2	17	-21	7	3	11	13	-18
2	0	2	153	140	1	1	7	24	23	9	1	5	22	-26	7	2	4	37	38	8	3	1	40	38
2	0	3	24	24	1	1	9	12	9	9	1	6	24	22	7	2	8	19	19	8	3	2	14	12
2	0	4	35	-27	1	1	11	26	-21	9	1	7	13	9	7	2	9	17	15	8	3	4	24	-18
2	0	5	44	-37	1	1	13	23	24	10	1	1	23	25	8	2	0	16	-19	8	3	7	15	11
2	0	6	87	-81	1	1	15	12	-8	10	1	3	17	-20	8	2	2	16	17	8	3	8	15	-8
2	0	7	29	-24	2	1	0	19	-22	10	1	9	12	-11	8	2	3	15	16	8	3	9	18	-23
2	0	8	52	45	2	1	1	75	87	11	1	3	15	-16	8	2	7	27	27	9	3	1	21	18
2	0	9	19	-14	2	1	2	19	-19	11	1	4	13	7	8	2	6	17	20	9	3	2	15	-9
2	0	10	22	-23	2	1	3	40	-43	11	1	5	15	18	9	2	2	23	20	9	3	3	18	-15
2	0	14	18	14	2	1	5	13	-10	12	1	1	14	-17	9	2	3	15	-19	9	3	4	19	-19
3	0	1	24	-21	2	1	6	14	-12	12	1	7	10	-12	9	2	6	17	18	9	3	5	19	18
3	0	2	84	81	2	1	7	34	35	0	2	2	76	-88	10	2	0	20	25	9	3	6	21	-13
3	0	3	56	50	2	1	9	50	-43	0	2	6	14	11	0	3	3	13	-13	10	3	1	18	-14
3	0	4	127	-123	2	1	10	17	19	0	2	8	39	39	0	3	5	19	-18	10	3	7	19	-22
3	0	5	18	-16	2	1	12	17	19	0	2	10	24	-19	0	3	7	48	49	11	3	3	14	12
3	0	6	16	20	2	1	15	12	-12	0	2	12	20	20	0	3	9	42	-41	11	3	5	15	-13
3	0	7	33	29	3	1	1	19	16	0	2	16	13	-11	0	3	15	11	-14	12	3	1	12	13
3	0	8	13	13	3	1	2	7	10	1	2	1	14	18	1	3	1	51	70	12	3	2	12	-7
3	0	9	21	-21	3	1	3	31	-33	1	2	2	13	-4	1	3	2	19	-19	0	4	6	22	19
3	0	10	33	-28	3	1	4	16	-10	1	2	4	10	-4	1	3	3	37	-39	0	4	8	41	-37
4	0	0	65	61	3	1	5	74	75	1	2	5	12	-12	1	3	4	10	8	1	4	2	33	-41
4	0	1	17	19	3	1	6	26	23	1	2	6	26	28	1	3	5	29	29	1	4	4	35	43
4	0	2	35	-31	3	1	7	17	-19	1	2	7	17	-15	1	3	6	11	13	1	4	6	33	-28
4	0	3	17	-17	3	1	9	14	-13	1	2	8	13	-10	1	3	9	28	-27	1	4	10	37	34
4	0	4	51	-47	3	1	10	16	17	1	2	10	37	35	1	3	11	27	29	2	4	0	33	-45
4	0	5	79	76	3	1	11	22	16	1	2	11	18	19	1	3	13	23	-24	2	4	2	41	50
4	0	6	58	-56	3	1	13	22	-24	1	2	12	24	18	2	3	0	23	-25	2	4	6	39	-42
4	0	10	22	17	4	1	0	10	-9	1	2	14	24	-24	2	3	1	55	-63	2	4	7	25	-19
4	0	14	18	-20	4	1	1	24	-23	2	2	0	28	-18	2	3	2	39	45	2	4	8	30	27
5	0	1	54	52	4	1	3	25	24	2	2	1	54	-65	2	3	3	18	20	3	4	2	30	37
5	0	2	59	-51	4	1	4	18	-16	2	2	2	37	-45	2	3	4	27	-26	3	4	4	55	-62
5	0	3	14	7	4	1	5	36	52	2	2	3	38	35	2	3	5	27	27	4	4	0	37	45
5	0	4	73	72	4	1	6	17	-15	2	2	4	32	33	2	3	6	25	25	4	4	2	31	-33
5	0	6	26	-29	4	1	7	29	-27	2	2	6	30	27	2	3	7	42	-42	4	4	6	33	32
5	0	8	19	-16	4	1	9	32	33	2	2	7	32	30	2	3	9	42	36	4	4	8	33	-28
5	0	10	24	27	4	1	11	17	-23	2	2	8	24	-22	2	3	12	15	-13	5	4	1	26	21
5	0	12	25	-26	4	1	13	13	-10	2	2	10	27	29	3	3	1	23	-22	5	4	2	30	-30
6	0	0	18	-20	4	1	15	11	12	2	2	16	11	12	3	3	3	47	48	5	4	4	43	46
6	0	2	30	27	5	1	1	9	6	3	2	2	10	-12	3	3	5	69	-66	5	4	6	31	-25
6	0	3	12	-9	5	1	2	22	17	3	2	4	50	56	3	3	7	18	15	6	4	0	32	-24
6	0	4	28	28	5	1	3	60	66	3	2	5	24	-23	3	3	8	13	-12	6	4	2	33	28
6	0	6	48	-54	5	1	5	39	-41	3	2	6	19	-21	3	3	9	15	13	6	4	6	30	-24
6	0	8	42	49	5	1	7	18	12	3	2	8	23	20	3	3	11	15	-14	6	4	8	28	27
6	0	10	18	-19	5	1	11	21	-19	3	2	12	19	-21	3	3	13	15	17	7	4	2	32	27
7	0	2	47	43	5	1	13	15	17	3	2	14	14	15	4	3	0	20	20	7	4	4	41	-37
7	0	4	53	-63	5	1	0	33	-31	4	2	0	35	-32	4	3	1	58	59	8	4	0	31	28
7	0	7	24	-26	6	1	1	20	20	4	2	1	40	38	4	3	2	17	-18	10	4	0	33	-28
7	0	10	16	-20	6	1	2	26	-24	4	2	2	37	35	4	3	3	45	-39					
7	0	12	18	19	6	1	3	16	-11	4	2	3	17	-16	4	3	4	30	26					
8	0	0	46	51	6	1	5	28	-27	4	2	4	18	-12	4	3	5	38	-31					
8	0	2	33	-36	6	1	7	38	38	4	2	5	13	8	4	3	7	21	22					

hydrogen atoms to the calculated structure factors have not been taken into consideration).

The correctness of the structure determined was tested by computing three-dimensional ( $F_o - F_c$ ) and  $F_o$  syntheses with all atoms included. The maximum value in the difference synthesis was 2% of the largest observed electron density value. Furthermore no value in the difference map was larger than  $\frac{1}{4}$  the value of a true carbon peak in the electron density map.

#### STRUCTURE DETERMINATION OF THE TRICLINIC MODIFICATION

*Unit cell and space group.* Crystals of the triclinic form of the 2,2'-dipyridyl complex with peroxochromic acid,  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{tric.})$ , have the following unit cell dimensions (reduced cell):

$$\begin{array}{ll} a = 9.212 \pm 0.009 \text{ \AA} & \alpha = 94.18 \pm 0.07^\circ \\ b = 8.773 \pm 0.004 \text{ \AA} & \beta = 92.13 \pm 0.08^\circ \\ c = 7.060 \pm 0.010 \text{ \AA} & \gamma = 108.78 \pm 0.06^\circ \\ V = 537.6 \text{ \AA}^3 & \end{array}$$

Observed and calculated  $\sin^2\theta$ -values are listed in Table 7.

Table 7. Observed lines in the powder diagram (Guinier focusing camera) of  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{tric.})$ .  $\lambda(\text{CuK}\alpha_1) = 1.54051 \text{ \AA}$ .

$h k l$	$10^4 \sin^2\theta_{\text{obs}}$	$10^4 \sin^2\theta_{\text{calc}}$	$d_{\text{obs}}$	$I_{\text{obs}}$
1 0 0	797	783	8.628	vst
0 1 0	871	867	8.253	vvw
1 $\bar{1}$ 0	1111	1113	7.311	st
0 0 1	1200	1202	7.031	vvw
0 1 $\bar{1}$	1882	1886	5.615	st
1 0 1	2123	2110	5.286	vst
2 $\bar{1}$ 0	2962	2926	4.476	w
1 $\bar{2}$ 0	3190	3178	4.313	st
0 2 0	3475	3468	4.132	st
1 $\bar{2}$ 1	4144	4138	3.784	vw
2 $\bar{2}$ 0	4462	4453	3.646	st
$\bar{1}$ 2 1	4626	4621	3.581	vvw
0 0 2	4804	4807	3.514	st
2 $\bar{2}$ 1	5546	5538	3.271	st
2 1 $\bar{1}$	5846	5843	3.186	vvw
3 $\bar{1}$ 0	6299	6305	3.069	w
1 1 $\bar{2}$	6407	6378	3.043	w
0 3 0	7825	7804	2.754	vvw
3 2 1	8493	8489	2.643	vvw
2 $\bar{2}$ 2	9040	9026	2.562	vvw
3 3 0	10039	10020	2.431	vvw
3 3 1	11423	11396	2.279	w
3 3 $\bar{2}$	11514	11512	2.270	w
2 4 0	12712	12710	2.160	vvw
4 4 1	19245	19248	1.7558	vvw
1 4 $\bar{2}$	19906	19897	1.7264	vw

Since it is possible to fit all the atoms into the unit cell in a centrosymmetrical manner, the space group is  $P\bar{1}$ .

The density of the crystals, as determined by the flotation method, is 1.755 g/cm<sup>3</sup>. The density for a unit cell containing two molecules is 1.779 g/cm<sup>3</sup>.

*Structure determination.* Patterson projections on (001) and (010) were calculated using  $hk0$  and  $h0l$  diffraction data. The chromium parameters were derived from the position of the largest peak in the two projections. Assuming  $P\bar{1}$  to be the correct space group with the chromium atoms occupying a general two-fold position the chromium parameters are approximately

$$x = 0.18 \quad y = 0.21 \quad z = 0.25$$

A structure factor calculation based on these coordinates gave an  $R$ -value of 0.48. The signs of the  $F$ -values thus obtained were used to calculate electron density projections on (001) and (010). From these projections approximate oxygen positions were obtained as well as the positions of the 2,2'-dipyridyl groups. It became obvious that the coordination about chromium was approximately the same as in the orthorhombic case, so that coordinates for all carbon and nitrogen atoms could be derived using these known distances and angles. A new structure factor calculation based on these positional parameters, using the temperature coefficients  $B$  obtained for the orthorhombic modification, was then performed, the resulting discrepancy factors being  $R_{hk0}=0.30$  and  $R_{h0l}=0.26$ . At this stage a refinement of the parameters was begun.

*Structure refinement.* Refinement of the parameters was performed by the structure factor least-squares method using the  $h0l$  and  $hk0$  reflexions and applying the block-diagonal approximation. The same expression for the weighting factor was used as in the orthorhombic case. As the ratio between the number of observations and the number of parameters was approximately 2:1 and as the diffraction data are neither complete nor of high quality it was evident that the refinement had to be carried out carefully. It was thus performed in the way normal in such circumstances, *i.e.* by refining minor

Table 8. Atomic coordinates (expressed as fractions of the cell edges) for  $[\text{Cr}(\text{O}_2)_2\text{dipy}](\text{tric.})$ .

Space group  $P\bar{1}$ . Two molecules in the unit cell. All atoms occupy the general two-fold position. Average standard deviations are given in the text.

Atom	$x$	$y$	$z$	Atom	$x$	$y$	$z$
Cr	0.1771	0.1988	0.2425	C <sub>2</sub>	0.693	0.152	0.306
O <sub>1</sub>	0.201	0.258	0.026	C <sub>3</sub>	0.707	0.189	0.166
O <sub>2</sub>	0.348	0.261	0.015	C <sub>4</sub>	0.841	0.441	0.177
O <sub>3</sub>	0.399	0.214	0.372	C <sub>5</sub>	0.956	0.380	0.092
O <sub>4</sub>	0.178	0.202	0.476	C <sub>6</sub>	0.106	0.504	0.277
O <sub>5</sub>	0.098	0.041	0.267	C <sub>7</sub>	0.162	0.662	0.190
N <sub>1</sub>	0.956	0.243	0.311	C <sub>8</sub>	0.318	0.701	0.198
N <sub>2</sub>	0.226	0.444	0.275	C <sub>9</sub>	0.402	0.698	0.200
C <sub>1</sub>	0.841	0.098	0.250	C <sub>10</sub>	0.404	0.572	0.338



groups of parameters in each cycle. The refinement converged, after several cycles, to the positional parameters given in Table 8. It was not considered profitable to refine individual isotropic temperature coefficients and these were assigned the same values as those obtained for the orthorhombic modification. The final  $R$ -values were  $R_{hk0}=0.15$  and  $R_{h0l}=0.19$ . Average standard deviations in the positional parameters given are 0.02 Å for Cr, 0.12 Å for O, 0.13 Å for N and 0.15 Å for C. The correctness of the structure was checked in the same way as for  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh.})$ .

## DESCRIPTION AND DISCUSSION

It has been demonstrated by the structure investigation that both the triclinic and orthorhombic modifications of  $[\text{CrO}(\text{O}_2)_2\text{dipy}]$  are composed of oxidodiperoxido-2,2'-dipyridylchromium(VI) molecules held together by van der Waals forces. One molecule is depicted in Fig. 1, the two nitrogen atoms in the dipy ligand being in the *cis*-position. The chromium atom is seven-coordinated in a similar manner to that of  $[\text{CrO}(\text{O}_2)_2\text{ophen}]$ , with the two peroxido groups and one nitrogen atom forming the equatorial plane of a pentagonal bipyramid and the other nitrogen atom and the oxide oxygen atom being situated at the apices. The equatorial plane of the bipyramid is planar in both forms within the limits of error, the equation of the plane, expressed

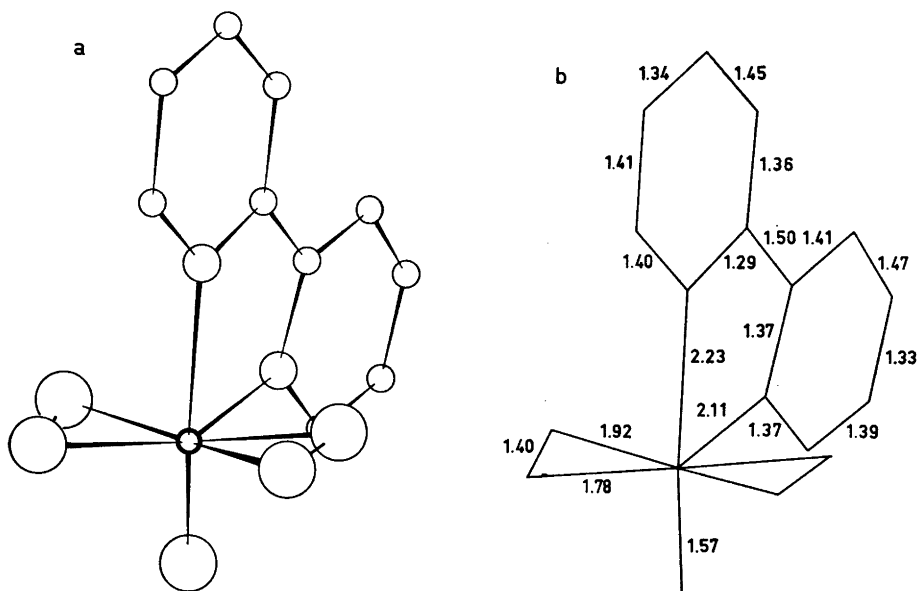


Fig. 1. The  $[\text{CrO}(\text{O}_2)_2\text{dipy}]$  molecule. (The circles in figure a represent, in order of decreasing magnitude, oxygen, nitrogen, and carbon atoms. The central atom is the chromium atom).

in fractional coordinates, being  $0.5453x + 0.8383z - 0.2722 = 0$  for the orthorhombic modification. The distances from the five equatorial atoms to this plane range from 0.01 to 0.02 Å. The chromium atom is displaced 0.31 Å (unless otherwise stated all distances and angles refer to the orthorhombic form) from the equatorial plane in the direction of the oxide oxygen atom, a situation similar to that found in other seven-coordinated peroxido compounds like  $[\text{CrO}(\text{O}_2)_2\text{ophen}]$ ,<sup>3</sup>  $\text{K}_2\text{Mo}_2\text{O}_{11}\cdot 4\text{H}_2\text{O}$ ,<sup>11</sup> and its tungsten analogue,  $\text{K}_2\text{W}_2\text{O}_{11}\cdot 4\text{H}_2\text{O}$ .<sup>12</sup> The dipy molecule is planar in the orthorhombic form since it lies in a crystallographic mirror plane and planar within the limits of error in the triclinic modification.

Bond distances and angles for  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh.})$  are given in Table 9 and packing distances in Table 10. In Table 11 mean bond distances for  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{tric.})$  are listed. The average bond distances and angles in the 2,2'-dipyridyl molecule found in this investigation together with those found by Merritt and Schroeder<sup>4</sup> are shown in Fig. 2. No significant differences are observed.

Table 9. Bond distances and angles in  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh.})$ .

	Distance (Å)	e.s.d (Å)		Angle (°)	e.s.d. (°)
Cr—O <sub>1</sub>	1.92	0.01	Cr—O <sub>2</sub> —O <sub>1</sub>	73.4	0.8
Cr—O <sub>2</sub>	1.78	0.01	O <sub>1</sub> —Cr—O <sub>3</sub>	99.8	0.3
Cr—O <sub>3</sub>	1.57	0.02	O <sub>2</sub> —Cr—O <sub>3</sub>	103.2	0.6
Cr—N <sub>1</sub>	2.11	0.02	O <sub>1</sub> —Cr—N <sub>1</sub>	88.1	0.3
Cr—N <sub>2</sub>	2.23	0.02	O <sub>1</sub> —Cr—N <sub>2</sub>	80.1	0.3
O <sub>1</sub> —O <sub>2</sub>	1.40	0.02	O <sub>2</sub> —Cr—N <sub>1</sub>	131.2	0.4
N <sub>1</sub> —C <sub>1</sub>	1.37	0.03	O <sub>2</sub> —Cr—N <sub>2</sub>	86.9	0.5
N <sub>1</sub> —C <sub>5</sub>	1.37	0.03	O <sub>3</sub> —Cr—N <sub>1</sub>	92.5	0.8
N <sub>2</sub> —C <sub>6</sub>	1.29	0.03	O <sub>3</sub> —Cr—N <sub>2</sub>	165.5	0.8
N <sub>2</sub> —C <sub>10</sub>	1.40	0.03	Cr—N <sub>1</sub> —C <sub>1</sub>	120.5	1.4
C <sub>1</sub> —C <sub>2</sub>	1.39	0.04	Cr—N <sub>1</sub> —C <sub>5</sub>	119.8	1.4
C <sub>2</sub> —C <sub>3</sub>	1.33	0.04	Cr—N <sub>2</sub> —C <sub>6</sub>	119.1	1.5
C <sub>3</sub> —C <sub>4</sub>	1.47	0.04	Cr—N <sub>2</sub> —C <sub>10</sub>	121.6	1.5
C <sub>4</sub> —C <sub>5</sub>	1.41	0.04	N <sub>1</sub> —Cr—N <sub>2</sub>	73.0	0.6
C <sub>5</sub> —C <sub>6</sub>	1.50	0.03	N <sub>1</sub> —C <sub>1</sub> —C <sub>2</sub>	121.0	2.2
C <sub>6</sub> —C <sub>7</sub>	1.36	0.03	C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	121.6	2.7
C <sub>7</sub> —C <sub>8</sub>	1.45	0.03	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	119.3	2.5
C <sub>8</sub> —C <sub>9</sub>	1.34	0.04	C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	117.0	2.4
C <sub>9</sub> —C <sub>10</sub>	1.41	0.04	C <sub>4</sub> —C <sub>5</sub> —N <sub>1</sub>	124.4	2.1
			C <sub>5</sub> —N <sub>1</sub> —C <sub>1</sub>	119.7	1.8
	Angle (°)	e.s.d. (°)	N <sub>2</sub> —C <sub>6</sub> —C <sub>7</sub>	123.9	2.1
			C <sub>6</sub> —C <sub>7</sub> —C <sub>8</sub>	121.5	2.2
O <sub>1</sub> —Cr—O <sub>2</sub>	44.1	0.5	C <sub>7</sub> —C <sub>8</sub> —C <sub>9</sub>	111.9	2.5
O <sub>1</sub> —Cr—O <sub>1</sub> <sup>1</sup>	160.1	0.5	C <sub>8</sub> —C <sub>9</sub> —C <sub>10</sub>	126.7	2.6
O <sub>1</sub> —Cr—O <sub>2</sub> <sup>1</sup>	132.4	0.6	C <sub>9</sub> —C <sub>10</sub> —N <sub>2</sub>	116.7	2.3
O <sub>2</sub> —Cr—O <sub>2</sub> <sup>1</sup>	90.0	0.6	C <sub>10</sub> —N <sub>2</sub> —C <sub>6</sub>	119.3	2.0
Cr—O <sub>1</sub> —O <sub>2</sub>	62.5	0.8			

Table 10. Packing distances in  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh.})$  less than 4.0 Å. The figures in parentheses refer to the generated positions as they appear in the *International Tables*, Vol. I (1952).

	Distance (Å)		Distance (Å)		Distance (Å)
$\text{O}_1-\text{C}_2$ (3)	3.82	$\text{O}_2-\text{C}_8$ (3)	3.39	$\text{C}_2-\text{C}_2$ (3)	3.99
$\text{O}_1-\text{C}_3$ (3)	3.25	$\text{O}_2-\text{C}_9$ (3)	3.63	$\text{C}_2-\text{C}_3$ (3)	3.78
$\text{O}_1-\text{C}_7$ (4)	3.43	$\text{O}_3-\text{C}_7$ (4)	3.73	$\text{C}_2-\text{C}_4$ (3)	3.53
$\text{O}_1-\text{C}_8$ (3)	3.62	$\text{O}_3-\text{C}_8$ (4)	3.87	$\text{C}_2-\text{C}_5$ (3)	3.55
$\text{O}_1-\text{C}_8$ (4)	3.99	$\text{O}_3-\text{C}_{10}$ (2)	3.39	$\text{C}_3-\text{C}_5$ (3)	3.78
$\text{O}_1-\text{C}_9$ (3)	3.42	$\text{N}_1-\text{C}_2$ (3)	3.79	$\text{C}_4-\text{C}_8$ (2)	3.99
$\text{O}_2-\text{O}_3$ (2)	3.76	$\text{N}_1-\text{C}_3$ (3)	3.53	$\text{C}_8-\text{C}_{10}$ (3)	3.79
$\text{O}_2-\text{C}_1$ (2)	3.22	$\text{N}_2-\text{C}_9$ (3)	3.83	$\text{C}_9-\text{C}_9$ (3)	3.73
$\text{O}_2-\text{C}_2$ (2)	3.66	$\text{C}_1-\text{C}_2$ (3)	4.00	$\text{C}_9-\text{C}_{10}$ (3)	3.45
$\text{O}_2-\text{C}_4$ (4)	3.45	$\text{C}_1-\text{C}_3$ (3)	3.52	$\text{C}_{10}-\text{C}_{10}$ (3)	3.73
$\text{O}_2-\text{C}_7$ (4)	3.64	$\text{C}_1-\text{C}_4$ (3)	3.55		

Table 11. Average bond distances in  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{tric.})$ .

	Number of measurements	Average bond distance (Å)	e.s.d. (Å)
Cr—O <sub>peroxido</sub>	4	1.8 <sub>1</sub>	0.1 <sub>1</sub>
Cr—O <sub>oxido</sub>	1	1.3 <sub>7</sub>	0.1 <sub>2</sub>
Cr—N	2	2.1 <sub>6</sub>	0.1 <sub>6</sub>
C—N	4	1.5 <sub>8</sub>	0.1 <sub>8</sub>
C—C	9	1.5 <sub>1</sub>	0.2 <sub>0</sub>
O <sub>1</sub> —O <sub>2</sub>	2	1.5 <sub>0</sub>	0.1 <sub>7</sub>

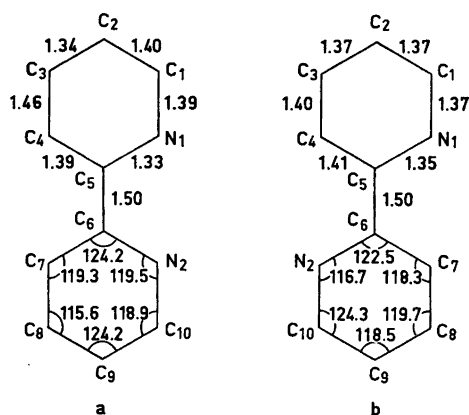


Fig. 2. Comparison of the interatomic distances and bond angles in the 2,2'-dipyridyl molecule found a) in the present work, and b) by Merritt and Schroeder<sup>4</sup> (1956).

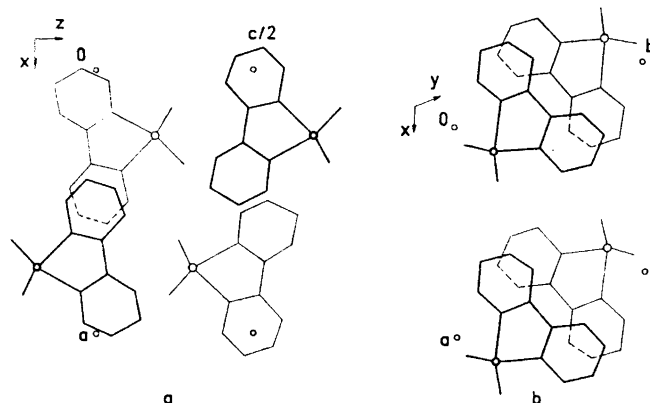


Fig. 3. Packing of the  $[\text{CrO}(\text{O}_2)_2\text{dipy}]$  molecules viewed down the shortest axis in the a) orthorhombic and b) triclinic modification.

The difference between the two forms lies in the way in which the molecules are packed together. This is evident from Fig. 3 which shows the projections of the contents of the unit cells of the two modifications along the shortest axes. No detailed comparison between the two forms is, however, possible at present since only approximate coordinates have been obtained for the triclinic form. It is, however, clear that the molecules are packed so that the 2,2'-dipyridyl planes are parallel to each other in the orthorhombic form and approximately so in the triclinic form, and that the perpendicular distance between these parallel planes is about 3.5 Å in both modifications.

The  $\text{Cr}-\text{O}_{\text{peroxido}}$  distances  $\text{Cr}-\text{O}_1$  and  $\text{Cr}-\text{O}_2$  are 1.92 Å and 1.78 Å, respectively and thus differ by 0.14 Å. In  $[\text{CrO}(\text{O}_2)_2\text{opphen}]$  the corresponding distances are 1.87 Å and 1.80 Å. There is therefore no significant difference between the corresponding  $\text{Cr}-\text{O}_{\text{peroxido}}$  distances in  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh.})$  and  $[\text{CrO}(\text{O}_2)_2\text{opphen}]$ . There was not previously thought to be a significant difference in the lengths of the  $\text{Cr}-\text{O}_1$  and  $\text{Cr}-\text{O}_2$  bonds in  $[\text{CrO}(\text{O}_2)_2\text{opphen}]$  but, in view of the result of this investigation, there may, however, in fact be a difference between them. Differences in the  $\text{M}-\text{O}_{\text{peroxido}}$  bond lengths are not usually encountered in this type of compound, although such a difference has been reported for  $\text{K}_3[\text{Cr}(\text{O}_2)_4]$  as a result of both crystal structure analysis<sup>13</sup> and ligand field calculations.<sup>14</sup>

The short  $\text{Cr}-\text{O}_3$  bond, 1.57 Å, indicates a bond order of approximately 2. A corresponding bond length of 1.56 Å has been observed in  $[\text{CrO}(\text{O}_2)_2\text{opphen}]$  and there is, thus, no significant difference in these bonds.

The  $\text{Cr}-\text{N}_1$  and  $\text{Cr}-\text{N}_2$  bonds are 2.11 Å and 2.23 Å, respectively, in  $[\text{CrO}(\text{O}_2)_2\text{dipy}](\text{o-rh.})$  and 2.11 Å and 2.26 Å in  $[\text{CrO}(\text{O}_2)_2\text{opphen}]$ . The results of the present investigation thus confirm the opinion already formed that the  $\text{Cr}-\text{N}_2$  bond is significantly weaker than the  $\text{Cr}-\text{N}_1$  bond, the latter being a normal single bond. It is, however, evident from the present investigation that the formation of the  $\text{Cr}-\text{N}_2$  bond is energetically more favourable than

a *trans*-configuration of the 2,2'-dipyridyl molecule, although this is the most stable configuration of the 2,2'-dipyridyl molecule in solid 2,2'-dipyridyl.

The bond distance between the oxygen atoms in the peroxido groups is 1.40 Å, which is identical with that found for  $[\text{CrO}(\text{O}_2)_2\text{o phen}]$ . An O—O distance shorter than the value 1.49 Å observed in single peroxides (see reference list in Ref. 1) and in  $\text{K}_2\text{Mo}_2\text{O}_{11}\cdot 4\text{H}_2\text{O}$  and  $\text{K}_2\text{W}_2\text{O}_{11}\cdot 4\text{H}_2\text{O}$  has also been observed in several other peroxidochromates.<sup>2,3,15-17</sup> The reason why this should be so has not yet been fully accounted for theoretically though a qualitative explanation has been proposed.<sup>1</sup>

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#### REFERENCES

1. Stomberg, R. *Arkiv Kemi* **24** (1965) 283.
2. Stomberg, R. *Arkiv Kemi* **22** (1964) 29.
3. Stomberg, R. *Arkiv Kemi* **24** (1965) 111.
4. Merritt, L. L., Jr. and Schroeder, E. D. *Acta Cryst.* **9** (1956) 801.
5. Wiede, O. F. *Ber.* **30** (1897) 2178.
6. Abrahamsson, S. and Larsson, K. *Arkiv Kemi* **24** (1965) 383.
7. Abrahamsson, S. *Arkiv Kemi* **24** (1965) 389.
8. Aleby, S. *Arkiv Kemi* **24** (1965) 395.
9. Larsson, K. *Arkiv Kemi* **23** (1964) 17.
10. Abrahamsson, S., Nilsson, B. and Selin, K. *Arkiv Kemi* **24** (1965) 407.
11. Stomberg, R. *Acta Chem. Scand.* **22** (1968) 1076.
12. Einstein, F. W. B. and Penfold, B. R. *Acta Cryst.* **17** (1964) 1127.
13. Stomberg, R. *Acta Chem. Scand.* **17** (1963) 1563.
14. Swalen, J. D. and Ibers, J. A. *J. Chem. Phys.* **37** (1962) 17.
15. Stomberg, R. *Arkiv Kemi* **23** (1965) 401.
16. Stomberg, R. *Arkiv Kemi* **22** (1964) 49.
17. Stomberg, R. *Arkiv Kemi* **24** (1965) 47.

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