Metal–Flavin Interactions: The Crystal Structure of Bis-(10-methylisoalloxazine) Silver Nitrite Tetrahydrate and Similar Disordered Nitrate–Nitrite

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A crystalline silver nitrite complex of 10-methylisoalloxazine (crystal I) and an isomorphous disordered nitrite-nitrate (crystal II) have been prepared and characterized by X-ray diffraction techniques. Both red crystals are monoclinic, with symmetry C2/c. The cell constants for crystal I are a=21.764 (11), b=7.005 (4), c=17.336 (9) Å, $\beta=107.57$ (2)°, Z=8, $\mu=60.9$ cm⁻¹, $\rho_{obs}=1.83$, and $\rho_{calc}=1.80$ g cm⁻³ with molecular formula $\frac{1}{2}$ AgNO₂. C₁₁H₃N₄O₂. 2H₂O. The final *R* for structure I, based on 588 countermeasured reflections, is $6\cdot2^{\circ}$. Crystal II with molecular formula $\frac{1}{2}$ AgNO₂. C₁₁H₃N₄O₂. 2H₂O. The final *R* for structure I, based on 588 countermeasured reflections, is $6\cdot2^{\circ}$. Crystal II with molecular formula $\frac{1}{2}$ Ag(NO₂)_{0.55}(NO₃)_{0.45}. C₁₁H₈N₄O₂. 2H₂O has cell constants a=21.732 (5), b=7.092 (2), c=17.503 (4) Å, $\beta=107.63$ (1)°, Z=8, $\mu=59.5$ cm⁻¹, $\rho_{obs}=1.80$ and $\rho_{calc}=1.78$ g cm⁻³. The final *R*, based on 1561 counter-measured reflections, is $6\cdot9^{\circ}$ %. In both structures each flavin binds to only one silver ion, using O(4) and N(5), the primary chelate site. The Ag⁺-O distances are similar [2-600 (9) Å in I and $2\cdot612$ (7) Å in II] but Ag⁺-N values differ [2.373 (9) Å in I and $2\cdot303$ (6) Å in II]. The flavin secondary chelate site is occupied by a water molecule, and N(3)H is hydrogen-bonded to a different water molecule. The silver atom, which lies on a twofold axis, exhibits coordination halfway between tetrahedral and square planar. The flavin-flavin dihedral angle is $40\cdot4^{\circ}$ in crystal I and $40\cdot1^{\circ}$ in crystal II.

Introduction

Flavoproteins form an important class of oxidationreduction enzymes. Perhaps the most important are those which participate in the electron transport system of mitochondria and couple the Krebs cycle with production of adenosine triphosphate (ATP) by serving as agents for the transfer of electrons from nicotinamide-adenine dinucleotides (NADH) or succinate to the cytochrome system (Wagner & Folkers, 1964). The flavin in metalloflavoproteins such as succinate dehydrogenase, NADH dehydrogenase and xanthine oxidase is assumed to interact with the metal atom or atoms at some point in the catalytic reaction. Because these proteins are usually complex, there is little definitive evidence. However, internal electron flow in xanthine oxidase is known to involve both metals and flavin with electrons moving from substrate to molybdenum to flavin to nonheme iron (Brady, Rajagopalan & Handler, 1971; Bray, 1971; Bray, Palmer & Beinert, 1965). Visible and ultraviolet absorption studies of model compounds in solution by Hemmerich and coworkers (Hemmerich & Spence, 1966; Hemmerich, Müller & Ehrenberg, 1965; Bamberg & Hemmerich, 1961) have shown that flavin in its semiguinone oxidation state binds many metals strongly, but that both the hydroquinone and quinone forms normally have little affinity for metals. The exceptions to this latter observation are Ag(I), Cu(I), Fe(II), and Mo(V) which do form complexes with quinoid flavins in various solvents, with accompanying shifts in the flavin spectra towards the red, an effect reminiscent of semiguinone formation. These workers have interpreted the selective metal affinity of quinoid flavin in terms of metal \rightarrow

flavin charge transfer (or backbonding) by easily oxidizable metal ions, with a resulting partial acquisition of semiquinone properties by the flavin.

Recently crystallographic studies of silver(I)-flavin complexes (Fritchie, Sproul & Wade, 1972; Fritchie, 1972a; Wade & Fritchie, 1973) and of a Cu(II) complex (Fritchie, 1972b) have shown that bond-length changes in quinoid flavins upon complexation with these ions are minimal or nonexistent, casting doubt upon this interpretation, and have also revealed two chelate sites within the flavin nucleus, a secondary site consisting of N(1) and O(2), as well as the primary site N(5) and O(4), originally suggested by Bamberg & Hemmerich (1961). The complexes studied here are of a different stoichiometry from any previous silver complex and thus give an opportunity to study further both the relative strengths of the two chelate sites and the question of metal \rightarrow flavin charge transfer.

Experimental

A hot, nearly saturated methanolic solution of silver nitrate was added to a warm solution of 10-methylisoalloxazine in formic acid and the solution allowed to cool and evaporate slowly, leading to crystals of type I. A second solution was prepared, identical with the first except for the addition of hydrogen peroxide (to prevent deposition of metallic silver). The morphology of the crystals prepared without peroxide (hereafter referred to as crystal I) was that of a hexagonal plate bounded by $\{100\}$, $\{010\}$, and $\{001\}$ with $\{001\}$ as the largest faces. The dimensions of the crystal used for data collection were approximately 0.20 mm along **a**, 0.13 mm along **b**, and 0.10 mm along **c***. Crystal I, however, appeared to be inferior in at least two respects: (1) there was some elemental silver deposited on the crystalline faces, and (2) intensity peaks measured on the Picker four-circle diffractometer were somewhat asymmetric, indicating poor crystalline formation. (Similarly, there was some streaking on Weissenberg photographs.) Therefore, a crystal from the peroxide-containing preparation (crystal II) was prepared for investigation. The type II crystal more commonly exhibited clear faces and a prismatic habit with a diamond cross section having $\{100\}$ and $\{001\}$ faces and truncated by {010}. The dimensions of the type II data crystal were approximately 0.10 mm along a, 0.20 mm along b, and 0.11 mm along c*. Because of the better quality of the peroxide crystal a more extended data set was collected.

Weissenberg photographs taken with Cu Ka radiation indicated monoclinic symmetry, a unit cell of about $21.7 \times 7.1 \times 17.5$ Å, and systematic absences characteristic of space group C2/c (*hkl* with h+k odd and h0l with l odd) for both crystals. It was not until more exact unit-cell measurements were obtained from counter-measured data that any discrepancy appeared between the two structures. Unit-cell constants for crystal I, refined by use of $\sin^2 \theta$ values determined on a Picker four-circle diffractometer with Cu Ka radiation ($\lambda = 1.5418$ Å) are a = 21.764 (11), b = 7.005 (4), c = 17.336 (9) Å, and $\beta = 107.57$ (2)°. With Z=8 and empirical formula $\frac{1}{2}$ AgNO₂. C₁₁H₈N₄O₂. 2H₂O, ϱ_{calc} is 1.80 g cm^{-3} . The refined cell constants for crystal II are a = 21.732 (5), b = 7.092 (2), c = 17.503 (4), and $\beta =$ 107.63 (1). With Z=8 and empirical formula $\frac{1}{2}$ Ag(NO₂)_{0.55}(NO₃)_{0.45}. C₁₁H₈N₄O₂. C₁₁H O₂. 2H₂O, ρ_{calc} is 1.78 g cm⁻³. Observed densities measured by flotation in a dibromoethane-carbon tetrachloride mixture were 1.83 g cm⁻³ for crystal I and 1.80 g cm⁻³ for crystal II.

The 55% nitrite-45% nitrate formulation for crystal II was deduced primarily from difference maps (see below), but elemental analysis data agree well with the formulation (experimental: $C=38\cdot20$, $H=3\cdot51$, $N=18\cdot28\%$; composition calculated for

 $\frac{1}{2}$ AgNO₂. C₁₁H₈N₄O₂. 2H₂O: C=38·71, H=3·52, N= 18·47 %; for $\frac{1}{2}$ Ag(NO₂)_{0.55}(NO₃)_{0.45}. C₁₁H₈N₄O₂. 2H₂O: C=38·26, H=3·48, N=18·26 %).

Intensities were measured with Cu $K\alpha$ radiation to a limit of $2\theta = 70^{\circ}$ for crystal I and $2\theta = 112^{\circ}$ for crystal II. The final refinement of crystal I used 588 reflections satisfying the criterion $I > 2\sigma_I$, while crystal II was refined with 1561 reflections satisfying the same criterion. All were measured by a 2θ scan of a card-controlled Picker 4-circle diffractometer with nickel-filtered Cu $K\alpha$ radiation and an Na(TI)I scintillation counter set to accept about 90% of the $K\alpha$ pulses. The scan range in 2θ was about 2° and two 20-sec background measurements were made for each peak. Standard deviations were calculated from the formula $\sigma_I = [C + (t_C/2t_B)^2(B_1 + B_2) + p^2I^2]^{1/2}$ where I = net intensity, C = scan count, B_1 and B_2 are background counts, t_C is the scan time, t_B is the time of each background count, and p=0.02. The data for crystal I were corrected for Lorentz, polarization, and absorption effects* (*International Tables for X-ray Crystallography*, 1968), the latter ranging from 0.38 to 0.59 in $|F_o|^2$. Likewise, Lorentz and polarization corrections were applied to the data of crystal II, but absorption corrections were deemed unnecessary owing to the roughly equidimensional cross-section of the crystal. UV-visible spectra were run on a Cary 14 spectrophotometer, the spectra of solids on powder mulled in stopcock grease and sup-

^{*} Major computer programs used were ORABS for absorption correction (Busing, Martin & Levy); LOKI, for solution and refinement (Fritchie); and ORTEP, for diagrams (Johnson).



Fig.1. Difference electron density in the anion planes. (a) Crystal I. (b) Crystal II. The crosses mark average atomic sites used in the refinement, and solid lines show possible locations of idealized nitrate and nitrite ions.

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Table 1. Po	

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Ag	1.0* 1.0*	-0.0217(2) 0.0435(2)	* *		C(6)	1-0492 (6) 1-0491 (4)	0-2111 (19)	0.1027 (8)	1.7 (3)
0 <i>W</i> (1)	0.6737 (9)	0.0187 (18)	-0.1840(9)		C(7)	1.0834 (5)	0-2723 (18)	0.0544 (7)	1.3 (3)
0 <i>W</i> (2)	0.7217 (4)	-0.2143 (17)	0.2026 (6)		C(8)	1-0537 (6)	0.3099 (19)	0.0209 (6) - 0.0273 (8)	2.1 (3)
~	0-7217 (3)	-0.2037 (15)	0-2011 (4)			1.0513 (4)	0-2142 (12)	-0.0312(5)	
NNit	* * - ~-	-0.0366 (40)	+ 4 -		C(9)	0-9855 (6)	0.2873 (19)	-0.0639 (7)	1.7 (3)
O(1)Nit*	$\frac{1}{2}$	-0.0347 (18)	$-\frac{4^{\circ}}{-0.2310}$ (7)			0.9868 (4)	0.2900(13)	-0.0623(5)	
11111/100	0.5463 (8)	-0.1851 (20)	-0.2298 (8)		C(74)	(.) $(.)$	$(11) \times (11) \times (11) \times (11)$	-0.010/(7)	0-8 (3)
O(2)Nit‡	*		1 -		C(10a)	0.8521 (6)	0.1174(20)	0-0076 (7)	1.5 (3)
	/7	0.0/42 (34)	4		VICION	(5) 8128 (3)	0.1204(13)	0.0043 (5)	í.
871111/11/0	0-5466 (21)	0.0338 (75)	-0.2425 (3)		(01)NI	0.8850(7)	0-1900 (11)	(0) 0.0390 - 0.0031 (0)	I·I (2)
N(1)	0-7896 (5)	0-0771 (17)	-0.0246 (6)	1-8 (2)	C(10)	0.8503(6)	0.2364 (20)	-0.1291 (8)	2.1 (3)
	0.7902(3)	0.0743 (11)	-0.0268 (4)		. i	0-8509 (4)	0-2262 (17)	-0-1267 (5)	
C(2)	0-7589 (8)	0-0025 (17)	0-0236 (10)	2-4 (4)	H(3)	0.7629	-0.0577	0-1365	3-0
0(2)	0.7012(5)	-0.0462 (13)	-0.0035(6)	3-1 (2)	H(6)	1.0698	0.1894	0.1539	3.0
	0.7006(3)	-0.0435 (11)	-0·0043 (4)						
N(3)	0.7876 (6)	-0.0288 (14) -0.0173 (11)	0.1054 (7)	1.9 (3)	H(7)	1.1293	0-2984	0-0715	3.0
C(4)	0-8500 (7)	0.0170 (17)	0.1432 (9)	1.8 (4)	H(8)	1.0753	0.3574	0.0652	3-0
	0-8507 (4)	0-0209 (12)	0.1411(5)					1))
O(4)	0-8755 (5) 0-8748 (3)	-0.0012 (11) 0.0085 (11)	0.2176 (7)	2.9 (3)	H(9)	0-9658	0-3173	-0.1170	3.0
C(4a)	0.8877 (6)	0.0897 (20)	0.0918 (8)	1-4 (3)	H(I)CH ₃	0-8643	0.1403	-0.1612	3.0
	0-8873 (4)	0.0930 (11)	0.0873 (5)						
N(5)	0.9486(4) 0.9487(3)	0-1199 (15) 0-1216 (10)	0.1225 (6) 0.1183 (4)	1-4 (2)	H(2)CH ₃	0.8618	0.3524	-0.1431	3.0
C(5a)	0-9819 (5) 0-9820 (3)	0.1895 (17) 0.1841 (11)	0.0701 (7) 0.0691 (5)	1.0 (3)	H(3)CH3	0-8045	0-2235	— 0·1364	3.0
			* These	parameters are fation factor is 0.	ixed by symmetry. 45 (nitrate) and 0.95	(nitrite)			
			t Popul	ation factor is 0-	45.				
			N LUPU	ALLON LACIOL IS V.	ou.				

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ported between silica plates. The background in the solid-state spectra (due to the stopcock grease) shows a slight rise toward the ultraviolet; this does not alter

the positions of the peaks, but causes a greater intensity in the ultraviolet peaks than would otherwise be observed.

Table 2. Anisotropic thermal parameters

The form of the thermal expression is $\exp \left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl) \right].$
For atoms Ag through O(1)Nit the first entry corresponds to crystal 1, the second to crystal 11 as in Table 1
Entries from $O(2)$ Nit to $O(10)$ correspond to crystal II only.

	B_{11}	B ₂₂	B_{33}	B_{12}	B_{13}	B_{23}
Ag	0.00132(5)	0.02635(54)	0.00205(8)	0*	-0.00027(11)	0*
8	0.00158(2)	0.02974(26)	0.00201(3)	0*	0.00074 (4)	0*
OW(1)	0.0063(7)	0.0454(49)	0.0057 (8)	-0.0028(23)	0·0017 (ÌÌ)	0.0135 (26)
	0.0069(5)	0.0546(34)	0.0047(5)	-0.0129 (19)	-0.0001(8)	0.0060 (20)
OW(2)	0.0011(3)	0.0462(40)	0.0055(5)	-0.0056 (17)	0.0011 (6)	0.0157 (23)
- (-/	0.0023(1)	0.0472 (27)	0.0050 (3)	-0.0024(11)	0.0019(3)	0.0082 (15)
NNit	0.0047 (9)	0.0858(127)	0.0034(12)	0*	0.0033 (16)	0*
	0.0073 (5)	0.0140 (28)	0·0047 (5)	0*	0.0071 (7)	0*
O(1)Nit	0.0035(3)	0.0545 (48)	0.0062(6)	-0.0009(25)	0.0035 (7)	-0.0011(31)
- (-/	0.0064(5)	0.0314(34)	0.0053 (5)	0.0107 (21)	0.0030 (9)	0.0063(22)
O(2)Nit	0.0105 (21)	0.001	0.0161 (32)	0*	-0.0103(42)	0*
O(1)NitD	0.0027(10)	0.0916 (187)	0.0110(26)	0.0046 (67)	-0.0016(24)	0.0266 (98)
N(1)	0.0013 (1)	0.0235 (19)	0.0019 (2)	-0.0008 (9)	0.0007 (3)	-0.0029(11)
C(2)	0.0017(2)	0.0061(15)	0.0037 (3)	-0.0013 (8)	0.0020(4)	-0.0017 (11)
O(2)	0.0013(1)	0.0345 (14)	0.0036 (2)	-0.0064(8)	0.0009 (3)	-0.0001 (11)
N(3)	0.0011(1)	0.0239 (18)	0.0021(2)	-0.0026 (8)	0.0013 (3)	0.0014 (10)
C(4)	0.0016 (2)	0.0163 (18)	0.0021 (3)	-0.0029 (9)	0.0015 (3)	0.0025 (11)
O(4)	0.0020(1)	0.0332(18)	0.0021(2)	-0.0041(9)	0.0011 (3)	0.0015 (10)
C(4a)	0.0013(2)	0.0077 (16)	0.0022 (3)	0.0010 (8)	0.0004 (3)	-0.0015(10)
N(5)	0.0010 (1)	0.0130 (14)	0.0020(2)	-0.0001 (8)	0.0003(3)	-0.0017 (10)
C(5a)	0.0011(2)	0.0088 (16)	0.0028 (3)	0.0001 (8)	0.0006 (3)	0.0018 (11)
C(6)	0.0011(2)	0.0202(22)	0.0037 (3)	0.0008 (10)	0.0009 (4)	0.0013 (15)
C(7)	0.0009(2)	0.0210(22)	0.0048 (4)	-0.0015 (10)	0.0018 (4)	-0.0011 (16)
C(8)	0.0022(2)	0.0096 (18)	0.0043(3)	-0.0014(9)	0.0039 (3)	-0.0009 (12)
C(9)	0.0013 (2)	0.0185 (20)	0.0030 (3)	-0.0002 (9)	0.0023 (3)	-0.0007 (13)
C(9a)	0.0015 (2)	0.0079 (15)	0.0028 (3)	-0.0013 (8)	0.0022 (3)	-0.0025 (10)
C(10a)	0.0008(1)	0.0174 (18)	0.0023 (3)	0.0023 (9)	0.0006 (3)	0.0002 (12)
N(10)	0.0008 (1)	0.0209 (17)	0.0019 (2)	0.0002 (8)	0.0008 (2)	0.0012 (10)
C(10)	0.0016(2)	0.0324 (27)	0.0022(3)	-0·0044 (11)	0.0016 (3)	0.0010 (14)

* These parameters are fixed by symmetry.

† Constrained to a small positive number.

Table 3. Observed and calculated structure factors for crystal I

Each group of three columns contains l, $10|F_o|$ and $10F_c$, and is headed by the values of h and k common to the group.

L FO FC	L FO FC	L F	0 F C	L FO	FC	L FD FC	L	۴D	FC	L FO	FC	L	FO	FC	ι	FO	FC	L	FD F0	ι	FU	۴C	t	FO	FC	ι	۶٥	۶٥
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•••	-3 789 855	9 28	302	-1 450	-324	• 0	- 4	585	\$29	7 212	-217	ē	690	135	~12	989	1012	-6	1345 -138		1961	2023		1/2	1//		228	-225
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3 856 -756	9 195 -111	-5 175	2 -1722	-6 1032	-972	8 1075 1015		•	3	-2 2411	-2231	-7	798	801		8	2			•	953	901	-4	1007	940	+6	•70	-452
4 1649 1907	10 596 -473	-> >2	2 3/8	-> 803	20-0	10 302 - 388				3 1854	1032		201	- 150					a 1	- 5	467	479	-2	1511 -	-1410	- 4	67?	62J
A ADR +627		-1 110	5 1530	-1 401	358	• •	- 13	164	- 6 3 7	4 1518	1521		701		-10	813	-897	-12		•	613	-560	<u>و</u>	445	-312	-?.	085	- 959
7 614 475	• •	-2 525	7 -5322	-1 340	-374		- 6	642	643	6 1 + 83	-1489	- 3	578	655	-9	353	- 390	-11	115 54		10		- 1	1300 -	1240		4.91	1433
8 1720 1710	-12 815 723	-1 255	2385	0 924	884	-12 740 040	- 7	358	304	8 1475	1443	- 2	848 -	- 827	-8	973	935	~15 1	225 -999			•	•		•//			1162
9 353 343	-11 219 -144	2 139	1 -971	1 1060	986	-11 308 -352		1186	-1251	10 955	-892	-1	173	-134	-7	607	659	- 7	489 -471	-5	209	-152		12	2		14	2
10 436 -424	-10 1098 -1048	1 72	• 744	2 538	-549	-10 1081 -1104	- 5	964	-286			0	577	598	-0	100	-635	-8	232 214	-4	510	596					•	•
11 160 -110	-9 984 -928	\$ 155	3 -1637	3 626	- 563	-9 198 -18.			435	\$	\$		•19	- 383	-?.	379	-439	-7	164 205	- 3	411	432	-10	574	-510	- 8	580	506
• •	-8 2094 2045		2 -147	6 1065		-0 1445 1524	;	201		-12 374	197	- 11	946 -	1035	- 31	205	1793	-6.4	321 -1953	-2	659	-671	-9	449	-401	-7	250	237
• •	-4 850 -931			6 228	183	-6 999 -102			-000	-11 245	-242		527	548	-21		-1301		1/3 103	-1	242	- 300	-8	715	684	-6	795	- 770
0 1590 1917	-5 1262 -1231	6 117	1 -1073	7 600	-639	-5 538 -54	i è	953	939	-12 581	-535		179	66	-1	647	-623		315 -228		120	307		317	305		376	-381
1 437 491	-4 400 436	7 20	3 161	8 615	634	- 520 501) I	710	865	-9 237	64	۰	905 -	-986	ō ı	382	1392	-21	832 -1685	•		,,,,	- 5	179	- 392	- 33	145	855
2 577 -655	-3 1170 1424	. 971	3 710	9 407	450	-3 158 -9	2	401	- 935	-8 1155	1553	,	338 -	-285	1	457	453	-11	201 1125		11	3		738	101	- 2	575	-572
3 240 -120	-2 1701 -1855	2 48	9 511			-2 329 26		548	-586	-7 693	734				21	1361 .	-1333	22	104 2059				- 3	275	281	-1	697	-732
4 700 776	-1 431 373	11 12 13	- 124	3	1	-1 163 -13		832	100	-6 221	-201		'			520	-570	1	901 835	-8	850	881	-2	587	-579	0	450	910
5 516 528	0 2585 2590	11 44		-12 1166	1174	1 1032 10	: :	733	-753	1 1 1 1 1 1	1591	-12	1185	1215		162	1031		711 -863		194	185	-1	540	-505	1	152	134
7 405 403	2 331 -282	,		-11 350	***	2 875 -81	ĩ	441	- 407	-3 522	631	-11	184	213	61	406 -	-1652		275 1351	- 22		- 6 4 2	0	147	728			
8 403 384	3 378 -412			-10 682	-68 t	3 1005 -100	. 8	926	861	-5 1190	-1737	-10	699 .	-696	7	100	-105	5	124 32		521	538	- 2 -	1221 -	-1266		15	1
	4 893 857	-5 +1	5 422	-9 360	259	4 2102 213				-1 189	-135	-9	117	-38	81	287	1317	5	885 -911	- 3	182	+182	- 11	205	-173	-8		
15	5 437 529	-7 52	\$ 543	-8 813	813	5 476 -37		5	ł	D 1815	1778	-8	818	857				7	145 -239	-2	270	- 339	- 4 I	1026	1104	- 7	94	20
	6 2041 -1968	-6 18	-935	-7 87		6 761 -71				1	009	-1	454	460			•	8	835 851	-1	612	- 587				-6	885	-867
-4 547 5/6	7 1212 1027	7	2 -700	-6 517	-453	8 1505 167		514	407		- 1 - 1		251	154	- 7	1 8 0					360	383		13	3	-5	426	- 456
-3 441 -713	9 831 774		2 243	-1 1127	1439	9 224 11	-12	969	- 952	÷ (333	1365	-4 1	1766	1702	- 6	824	+906		13 3	-	181	- 83					639	631
-1 516 -562	10 460 -476	-2 28	1 -184	-3 902	936	10 1044 -106	9	542	-483	5 541	513	- 3	288	-261	-5	469	-531	-12 1	195 1228		120	- 111		334	- 334	- 3	169	127
0 478 541	11 154 -89	-1 53	1 -743	-Z 1874	-1916		-8	493	958	6 1052	-1034	-21	1250 -:	1241	-4	815	868	-15	997 -917					726	724	11	225	1 3 2 9
1 317 252	12 528 517	2 35	3 315	-1 294	289	• •	- 7	551	640	7 292	-350	-1	020 .	-650	-3	208	195	-8	593 636		11	1	-3	232	105	ò	815	
2 549 -587		1 52	5 504	2 636	532			1515	-1251	8 565	531		1953	1812	-2	749	-847	-6 1	285 -1266				-2	218	171	ī	292	306
3 464 -429	. 25	2 58	5 -579	1 8/2	84/	-8 447 53	5	0/2	- 551	4 413	***	÷.	483	870	-1	330	-324		317 1124	-11	266	-260	-1	\$38	-570			
4 347 366		2 41	3 -383	2 1414	-1202	-/ 18/ -0		111				- ('	150	1853		140	885	- ? 1	005 -984	-10	628	-959	0	1048	1068		16	0
	-10 1966 -191			4 1066	999	-5 1394 -152	1 -2	1056	-1029	-			2254	2093	ż	991 .	-1122	2	821 -821	-9	1002	1507						
	-8 1956 1938		-526	5 971	766	-4 1013 113	+ -1	817	-175	-8 408	434	5	166	-03	3	783	-814		793 1721	-7	257				•	-6	140	-801
-10 1324 -1339	-6 3252 -3062	1 2	1 -233	6 878	-872	-3 1359 -138	2 0	657	680	-7 359	344	6.1	1441 -1	1353				6 1	715 -1721	-6	1150	-1232	-10	774	- 720	- 22	21	1234
-9 268 -267	-4 2557 2590)		7 411	358	-2 643 63	9 1	829	-540	-6 537	-613		201 -	-214		9	3			-5	102	79	-8	649	681	-2	.,,	-114
-8 613 625	-2 2277 -2557	' 1	5	8 607	667	-1 1206 -125	: ?	137	-111	-> >>	-525	8 1	1153 1	1515					12 5	-6	1367	1383	-1	222	194			
-7 282 269	0 2105 2143			9 235	233	0 /72 74	: ?	840	573		-244		1+0 -	-139	- 10	419	-386			-3	689	783	-0	674	-047			
-6 962 -951	Z 1044 -933	, -6 76	1010	10 195	-/84			***	400	- ,	,,,				- 4	410	-436	-11	215 -259	-2	1615	-1582	- 5	362	415			

Structure solution and refinement

Both structures were solved by Patterson and Fourier techniques. When it was realized that they were genuinely different, the decision was made to refine and report both, because of the rarity (if, indeed, not lack of precedence) of such a case and because of the opportunity to study the effect of the relatively small crystal-structure perturbation on the geometry of the complex. Owing to the high ratio of parameters to reflections only the non-flavin atoms were given ellipsoidal temperature factors during refinement of crystal I, whereas all atoms except hydrogen were allowed anisotropic vibrational models in crystal II. In crystal

Table 4. Observed and calculated structure factors for crystal II

Each group of three columns contains l, $10|F_a|$ and $10F_c$, and is headed by the values of h and k common to the group.

L FO	۶C	L F0	FC	L FO	FC	1 FO	FC	L FO	FC	L FO	۴c	ι	FO F0	ι	FO	FC	L F0	FC	ι,	0 FC	ι	FC	FC	L F0	FC	ι	FO	FC
0 4 3091 6 1420	0 2914 -1392	-10 957 -9 515 -8 2060 -7 303 -6 817	-927 -419 1968 -279 -790	4 210 5 338 6 238 7 341 8 210	-140 -309 97 335 -90	-13 192 -12 661 -11 842 -10 943 -9 581	67 676 -848 -955 597	4 568 5 826 6 531 7 478 8 651	592 -834 -552 525 707	-10 95 -9 266 -8 222 -7 181 -6 189	9 298 -248 -148 -227	-17 5	8 2 11 51 22 -11	10 11 12	303 772 343 9 1	289 806 387 -	11 12 128 11 157	5 20 -101	10 64 11 39	8 -678 9 333 4	8 10	615 1135 664	-612 -643	-2 653 0 749 2 828 4 817 6 700	-656 724 -857 829 -720	-2 -1 -1 -1 -2 -2 -2 -1 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	92 - 178 235 566 -	468 121 236 568 745
8 1922 10 450 12 545 14 634	1869 -492 556 -645 678	-5 654 -4 353 -3 535 -2 1628 -1 1198	-583 414 451 -1794 1112	9 307 10 199 3	-267 111 5	-8 1288 -7 769 -6 904 -5 374 -4 410	1271 -808 -894 447	9 467 10 514 11 441 12 584 13 480	-456 -501 428 595 -489	-5 816 -4 434 -3 186 -2 211 -1 452	881 -585 195 -170 527	-15 1 -14 4 -13 5 -12 6 -11 6	57 6 07 -41 55 56 04 62 92 -69	-18 -17 -15	517 - 555 202 - 452	547 549 246	10 185 -9 352 -8 251 -7 404 -6 121	-153 359 234 -410 -125	-14 14 -13 40 -12 17 -11 18 -10 54	6 -133 4 429 7 -133 3 -181 5 -574	-16 -15 -14 -13	173 195 - 286 - 323	184 158 295 321 ~	8 438 16 15 130	444 2 -57	3	147 214 369 -	-71 202 -371
0 1241	2	0 2185 1 155 2 205 3 387	2441 194 -175 307 721	-13 476 -12 707 -11 224 -10 442	476 793 -124 453	-3 774 -2 418 -1 935 0 842	-653 374 958 967	14 222	-231 1	0 112 1 415 2 196 3 402	-74 -413 244 462	-10 6	52 -711 77 420 69 -17	-14 -13 -12 -11 -10	865 - 288 513 201 - 1006 -	878 272 547 151 984	-5 343 -4 189 -3 250 -2 270 -1 292	342 167 -265 -335 260	-9 69 -8 21 -7 46 -6 22	9 753 0 205 9 -497 0 -168	-12 -11 -10 -9 -8	567 372 - 513 - 353	613 - 352 - 530 - 329 -	4 117	68 427 528 47	-10 -9 -8 -7	24 - 88 130	199 193 88
2 2145	-2090 139 1455 -744 -433	5 276 6 1883 7 1590 8 584 9 418	-212 -1862 1465 641 373	-8 230 -7 446 -6 189 -5 637	118 -445 27 659	2 755 3 107 4 1870 5 1328	-817 147 1952 -1345	-17 202 -16 558 -15 167 -14 700	201 613 -101 -756	5 115 6 126 7 289 8 90	-81 126 324 -90	-5 5 -4 14 -3 7 -2 11	94 59 67 139 89 -77 71 -118	-9 -8 -7 -6	105 144 125 1928 -1 327	-57 186 -88 875 295	0 132 1 453 2 132 3 332 4 166	-90 -460 -138 341 109	-4 29 -3 37 -2 17 -1 53 0 25	7 286 5 -398 3 -75 3 567 8 282	-7 -6 -5 -4	373 - 638 - 291 575 683 -	370 699 302 560	9 285 8 350 7 245 6 311	292 351 -200 -287	-6 -5 -4 -3	83 - 105 179 191 - 155 -	189 295 269 388 246
7 1361 8 1461 9 38 10 20 11 60	1358 1481 -367 -256 604	10 443 11 334 12 507 13 297 14 450	-464 185 491 -228 -489	-3 546 -2 427 -1 467 0 222 1 480	-545 303 457 124 -447	7 277 8 1376 9 599 10 907 11 485	240 1435 -638 -932 410	-12 332 -11 141 -10 1023 -9 144 -8 1095	336 104 -1042 -70 1128	7 -13 276 -12 127 -11 278	5 333 11 -299	0 11 1 5 2 11 3 4	36 118 52 -53 52 -125 62 53	-4 -3 -2 -1	1475 1 676 - 1596 -1 1553 1 1885 1	523 639 614 461 843	5 355 6 149 7 276 11	-373 -103 301	1 44 2 15 3 43 43 44 5 34	3 -443 5 -79 5 464 3 39 2 -352	-2 -1 0 1 2	420 - 105 763 542 - 495 -	445 -65 764 529 487	4 820 3 140 2 801 1 536 0 673	823 -162 -823 503 713	-1 0 1	22 10 38 -	202 31 454
12 820 13 41 14 46 15 26 16 25	849 -385 -504 230 248	15 267 16 507 17 192 2	162 533 -76	2 372 3 512 4 138 5 374 6 127	-379 558 41 -385 -116	12 531 13 404 14 720 15 465	533 -304 -776 458	-7 135 -6 1283 -5 231 -4 365 -3 479	70 -1268 -217 354 -435	-10 121 -9 247 -8 139 -7 404 -6 132	50 313 111 -372 25	5 6 6 12 7 6 8 11 9 1	07 -77 05 -128 85 65 04 110 11 -7	1 2 3	455 582 - 1043 1110 1 369 -	393 648 - 993 - 132 - 339 -	16 637 15 384 14 220 13 278	728 -374 -223 281	6 29 7 48 8 13	6 -237 494 114	34567	413 583 380 - 561 - 180	420 597 375 571	1 449 2 700 3 449 4 561 5 148	-441 -720 436 602 -107	-11 -10 -9 -8	42 - 77 - 68	102 339 517 184
17 354 0 0 1225	-351 4 1269	-18 342 -16 527 -14 934 -12 866	-341 546 -940 951	7 475 8 102 9 345 10 157 11 292	511 -40 -379 -141 269	4 -15 391 -14 271 -13 452	- 349 - 231 - 416	-2 846 -1 307 0 425 1 1255 2 495	-861 -337 508 -1211 -583	-5 499 -4 122 -3 389 -2 249 -1 527	478 -64 -393 -251 589	16 3 11 9 12 4 13 2	179 -41 28 52 15 42 90 -27	6 7 8 9	782 - 263 726 222 - 431 -	826 -1 212 -1 730 -1 135 -	12 362 11 459 10 521 -9 137 -8 779	368 -515 125 800	-8 15 -7 24 -6 10 -5 22	89 -236 104 195	\$	884 407 - 14 4	681 438	6 561 7 411 16	- 587 407 4	-7 -5 -4 -3	95 - 164 - 176 27 161 -	160 367 300 214 273
1 620	-694 -341 912 483 -443	-10 1875 -8 2018 -6 3669 -4 2838 -2 2623	-1900 2047 -3343 2629 -2280	12 79 3 -16 347	3	-12 711 -11 279 -10 282 -9 479 -8 290	747 -232 161 473 275	3 1242 4 822 5 526 6 1498 7 243	1135 886 -501 -1576 247	0 373	383 -513 -365 495 321	-15 2 -14 1 -13 3	8 4 95 -29 42 -9	13	150 160 10 0	-91	-7 524 -6 555 -5 318 -4 373 -3 769	-513 -531 319 404 -762	-3 11 -2 22 -1 36 -14	80 -82 297 3 356 7 -30	-13 -12 -11 -10 -9	187 249 - 515 - 375 - 329	89 - 151 - 488 - 349 - 261 -	2 126 1 383 0 119 9 316 8 295	73 -397 -115 302 284	-2 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1	99 10 -	222 307 186 448 460
7 50 8 18 9 60 10 21	-188	2 1112 4 371 6 3136 8 272	-1258 449 -3209 310	-14 415 -13 575 -12 605 -11 242	-472 565 629 -206	-6 335 -5 487 -4 820 -3 2204	-249 -399 795 -2195	9 286 10 1151 11 293 12 851	-255 -1196 270 866	5 131 6 131 7 391 8 114 9 525	-174 -174 -38 -556	-12 1	53 -38 53 -3 57 51 12 19	-18 -16 -14 -12 -10	305 - 338 917 - 1079 1	309 387 965 131	-1 210 0 220 1 705 2 386	238 205 -717 -326	2 12	5 - 55 5	-7	404 - 255 - 341 380 -	362 207 338 336	6 251 6 912 4 563 3 109	272 969 598 -62	-14 4	9 1 46 - 56	497
12 10 13 28 14 17 15 30	58 -279 -157 332	12 1002	977 -477 899	-9 910 -8 461 -7 415 -6 834 -5 499	873 465 -393 -874 474	-1 278 0 525 1 758 2 446	-182 531 -837 -454	15 261 6	0	-17 276	3		98 -46 27 52 61 47 62 -88	-8 -6 -2	484 1296 -1 1316 1 995 -1 847	532 234 393 009 902	4 303 5 513 6 521 7 388 8 361	215 -551 -551 346 391	-10 12 -9 38 -8 15 -7 19 -6 21	-141 411 74 -175 -221	-2 -1 0 1	453 - 471 319 576 -	400 - 479 259 560 256	1 490 0 255 1 223 2 129	501 222 -210 119	-11 4 -10 4 -9 5 -8 6	78 - 41 - 10 - 39	288 250 531 886 888
0 144 1 309 2 123	6 -321 81	-17 341 -16 429 -15 378 -14 361	271 416 -321 -316	-4 1756 -3 1047 -2 669 -1 1110 0 587	1805 -1003 -443 1090 627	4 268 5 658 6 259 7 444 8 337	255 -707 -234 447 332	-16 1387 -14 166 -12 1111 -10 1278 -8 977	1524 -120 1196 -1296 1063	-15 404 -14 274 -13 151 -12 382 -11 441	-419 -264 100 432 -455	-1 6 0 3 1 9 2 6	82 72 846 36 900 -98 113 -60 213 23	2 6 8	773 - 1647 1 1486 -1 259 - 818 -	846 573 1 453 1 218 839	9 191 10 289 11 403 11	-199 -293 402	-5 17 -4 43 -3 43 -2 35 -1 37	151 -454 -458 -300 371	14567	637 169 - 193 - 538 - 484	645 102 167 590 517	4 483 17 6 99	502 5 -79	-6 -5 -6 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3	01 - 42 - 03 89 42 -	699 421 204 25 424
3 41 4 9 5 35 6 11 7 32	456 12 -385 108 339	-13 466 -12 480 -11 409 -10 1211 -9 900	391 494 -359 -1244 836	L 380 2 270 3 659 4 726 5 1440	-351 -317 628 724 -1464	9 439 10 242 11 507 12 348 13 529	-467 -178 473 350 -524	-6 522 -4 464 -2 2472 0 1788 2 1740	-618 487 -2441 1817 -1768	-10 458 -9 562 -8 784 -7 131 -6 108	-499 529 757 -143 -97	6 1 6 1 7 3	116 6 125 -79 193 -20 377 40 269 29	-17	635 10 2 257	-1 -1 -1 262 -1	18 255 17 122 16 483 15 260	-275 48 491 -228	0 11 1 35 2 13 3 27 4 17	91 -377 -32 277 3 130	-10	15 5 103 234	-18	5 214 4 138 3 334 2 165	220 143 - 331 - 135	-1	152 141 190 156 -	380 768 41 325 368
9 213 10 114 1	-121 -199 -26	-8 88 -7 692 -6 1542 -5 1507 -4 998	-664 -1504 1452 894	6 387 7 349 8 519 9 420 10 399	348 468 61 -413	-11 363 -10 222	6 - 340 159	4 1598 6 1467 8 1427 10 954 12 938	-1483 1443 -897 960	-5 761 -4 480 -3 481 -2 614 -1 951	-485	10 1	8 6	-15	233 - 589 - 347 603 -	208 -1 508 -1 508 -1 506 -1 506 -1	13 223 12 8C0 11 470 10 552	-526 189 797 -463 -601	-16 21	3		130 254 - 322 - 154 442 -	57 282 -1 133 -1 454 -1	17 3 340 2 252 1 244	3 374 280 -208	5	45 10 0	-82
-13 27 -12 18 -11 52 -10 23 -9 30	271 69 -548 -222	-2 5448 -1 3790 0 1200 1 233 2 1300	-5044 3518 -1188 -181	12 412 13 393 14 435 15 326	417 -363 -437 327	-8 223 -7 301 -6 249 -5 780 -4 261	-102 -271 -230 805 -173	-17 352 -16 397	2	1 1297 2 1160 3 119 4 322	-1270 -1198 164 368	-9 2	239 23 123 1 291 -30 162 18 236 19	-10	225 - 103 1715 1 773 - 922 -	82 82 702 741 936	-8 1523 -7 539 -6 1060 -5 357 -4 1213	1453 -488 -1082 301 1196	-14 29 -13 32 -12 16 -11 18 -10 51	-299 328 141 -188 -505	-2	701 - 251 134 309 -	754 234 52 350	9 340 8 390 7 140 6 127 5 791	322 403 -55 -106 776	-10 -8 1 -6 -4	58 94 1 74 84	-80 623 248 466
-8 13 -7 38 -6 26 -5 51 -4 23	5 118 5 -402 7 -235 1 532 5 172	3 754 4 620 5 720 6 899 7 871	676 629 -729 -968 795	3 -18 247 -17 239 -16 666	1 -399 164 663	-3 274 -2 303 -1 417 0 189 1 385	175 398 427 57 -363	-15 258 -14 636 -13 185 -12 164 -11 686	-249 -660 95 136 -718	6 68 7 45 8 510 9 50 10 45	-692 474 513 -483 -480	-4 -3 -2 -1 -1 -2 -1 -1 -2 -1 -	112 4 356 -36 -87 10 260 30	-5	668 1077 1 680 - 936 -1 614	591 - 084 - 714 - 010	-3 3G6 -2 1476 -1 646 0 167 1 404	283 -1437 599 -132 330	-9 47 -8 19 -7 33 -6 23 -5 27	483 197 -362 -224 275	-15	15 3 217 - 180 -	244	4 986 3 130 2 198 1 218 0 283	1037 -60 -182 217 270	2	04 1 38 0 2	018
-3 71 -2 31 -1 49 0 15 1 61	-765 -317 505 5113 -695	8 604 9 310 10 638 11 334 12 525	624 -272 -685 238 525	-15 193 -14 669 -13 194 -12 1076 -11 170	-670 -670 71 1096 61	2 233 3 387 4 192 5 379 6 195	227 393 -73 -358 74	-10 383 -9 852 -8 1014 -7 116 -6 147	-404 856 996 -116 -139	11 208 12 321 13 497 7	1 159 1 347 9 -519 1	231	2C4 28 173 16 128 A 332 -33	0 1 1 2 3 4 1 4 1 4 1 4 1 4 1 4 1 4 1 4 1 4 1 4	1422 1 221 284 - 748 784	410 138 327 764 808	2 977 3 568 4 839 5 666 6 1125	-1005 542 884 -677 -1118	-4 61 -3 46 -2 23 -1 22 0 89	617 -435 272 225 920	-13 -12 -11 -10	159 175 370 - 276 - 178	119 166 375 263 128	1 576 2 427 3 219 4 339 5 433	-614 -442 191 316 -443	-12 -11 -10 -9 -8	155 101 115 - 113	364 -40 346 286 471
2 22 3 44 5 51 6 19 7 39	-188 503 -514 55 378	13 362 14 581 15 420 16 500	-314 -640 407 535	-10 709 -9 783 -8 824 -7 583 -6 694	-692 749 864 -519 -754	7 256 8 196 9 342 5	-73 -305 5	-5 1781 -4 1464 -3 489 -2 1580 -1 962	1639 1444 -472 -1563 999	-18 336 -17 39 -16 /69 -15 609	-407 394 800 622	-13 2	118 13 9 5 246 24	, , , , , , , , , , , , , , , , , , ,	285 - 499 - 349 769 129 -	521 312 786 1	7 510 8 179 9 862 10 1122 11 166	-129 -874 -1131 98	1 56 2 46 3 56 4 26 5 20	-533 -492 591 239 -186	-8	351 154 - 268 946 611	330 164 251 951 -1 601 -1	17 5 83 4 325	1 -36 -338	-7 -6 -5 -4 -3	75 - 66 - 45 46 41	254 162 218 464 -80
9 42 10 19 11 310 12 19	-426 61 283 101	-15 314 -14 139 -13 751	-326 -78 798	-5 143 -4 1405 -3 250 -2 1871 -1 926	1473 201 -1746 964	-13 367 -12 342 -11 291 -10 228	369 297 -292 183	0 1544 1 418 2 1284 3 726 4 1147	1536 -448 -1344 705 1180	-14 36 -13 65 -12 105 -11 200 -10 66	311 643 1040 -165 1 -655	-12 -11 -10 -9 -8	80 1 255 -26 102 -5 367 38 223 17	11	599 577 10 4	614 655 -1	12 554	0 -538	7 53 8 45 9 43	-423 533 482 -419	-1	195 - 451 - 397 394 409 -	449 - 388 - 399 - 420	2 455 1 110 0 425 9 203	187 480 21 -448 -139	-2 -1 1 2	20 - 67 47 902 - 38 -	349 537 452 162 228
-16 25 -15 38	3 160 -382 -150	-12 34 -11 160 -10 434 -9 921 -8 190 -7 42	-135 -435 943 114	1 155 2 1155 3 735 4 924 5 324	91 -1173 -673 950 279	-9 337 -8 246 -7 478 -6 597 -5 549 -6 368	142 -443 -597 552 -328	6 878 7 507 8 482 9 352	-954 477 519 -296 -872	-8 d3 -7 17 -6 36 -5 70	787 1 124 313 5 648	-5	215 -17 342 32 377 34 432 -43	2 -15 8 -14 5 -13 6 -12 6 -11	398 211 - 492 220 343 -	425 -1 205 -1 486 -1 181 -	14 425 12 678 10 1169 -8 872 -6 967	-482 699 -1210 877 -988	-17 9 -16 39 -15 15 -14 51	-51 5 406 7 -66		728 122 196 963 -1	761	7 1020 6 1020 5 329	-1033 -1031 -297 710	-7	38 96 -	-61
-13 39 -12 34 -11 31 -10 100	359 250 -284 -1062	-6 538 -5 353 -4 1144 -3 880 -2 230	-529 312 1116 -926 -127	6 693 7 734 8 552 9 258 10 724	-716 742 613 -231 -719	-3 354 -2 146 -1 341 0 207 1 407	-360 38 334 109 -399	11 387 12 879 13 357 14 438	352 902 -350 -464	-3 75 -2 109 -1 11 -1 11 -1 11 -1 11	-750 -1136 -1C1 2 1785 406	-1	485 46 236 26 284 -31 411 40 193 18	-10 7 -9 6 -8 8 -7 2 -6	327 - 451 233 412 - 361 -	325 - 446 - 231 433 329	-4 999 -2 1451 0 467 2 1185 4 498	1120 -1397 -390 -1162 516	-13 23 -12 69 -11 16 -10 67 -9 21	225 732 5 70 -685	-16	15 1 285 137	291	2 497 1 285 0 668 1 271 2 644	-531 323 674 -235	-4	119 11 1 135	325
-8 39 -7 90 -6 62 -5 91 -4 59	357 -930 -633 893 603	-1 23 0 25 1 494 2 35 3 61	201 -136 -524 -359 648	11 306 12 823 13 239 14 749 15 505	277 860 -158 -739 515	2 190 3 1027 4 212 5 223 6 241	-61 1081 73 102 -168	6 -15 292 -14 237 -13 325	4 -284 -229 318	2 175 3 37 4 197 5 52 6 124	7 -1774 9 417 7 1993 1 -555 0 -1256	5 6 7 8	289 -32 89 2 402 44 154 16 316 -30	3 -5 0 -4 0 -3 0 -2 0 -2	690 282 507 - 369 - 591	709 245 531 1 360 1 634	6 751 8 224 10 1315 12 754	-788 181 -1351 750	-8 58 -7 12 -6 58 -5 59 -4 56	598 -101 -610 590 589	-14 -13 -12 -11 -10	366 - 318 356 222 - 391 -	397 304 361 173 409	3 149 4 735 5 141 6 377 7 221	79 727 86 - 370 203	-11 -10 -9 -8 -7	11 - 99 - 22 61 71 -	223 303 -53 565 355
-3 70 -2 161 -1 160 0 56 1 81	-643 2 -1663 5 1486 2 652 1 -848	4 201 5 594 6 288 7 661 8 211	111 -616 -245 681 124	16 846 4 -18 544	912 0 -586	7 511 8 304 9 364 10 233 11 286	516 238 -351 -162 417	-12 112 -11 364 -10 185 -9 615 -8 206	-43 -393 -141 664 204	7 29 8 99 9 36 10 81 11 27	7 292 2 1008 5 -352 2 -796 8 264	-16	9 3 202 20 267 - 76	0 12 1	309 567 203 - 612 270	294 630 167 -1 621 -1 206 -1	12 17 170 16 490 15 382	2 124 527 -324	-3 49 -2 33 -1 51 0 94 1 18	-489 -382 468 970 -199	-9 -8 -7 -6 -5	261 413 257 - 784 - 162 -	234 447 215 803 - 119 -	18 4 735 12 211	0 -806 144	-6 -5 -4 -3 -2	47 140 116 123	-74 90 291 54 587
2 80 3 51 4 125 5 52 6 81	-853 474 1309 2 -516 -862	9 492 10 371 11 551 12 251 13 395	-553 -398 542 3 234 -391	-16 687 -14 824 -12 1380 -10 1332 -8 1627	703 -899 1402 -1396 1566	5 -17 281 -16 250	3 265 210	-7 559 -6 457 -5 274 -4 414 -3 600	-515 -413 282 -417 -639	12 52 13 39 14 35 15 19	3 -372 3 -357 3 161	-14 -13 -12 -11 -10	302 -32 403 44 267 27 478 -50 230 -20	1 7 6 10	203 - 498 176 289 -	192 - 504 - 208 - 306 -	14 343 13 351 12 549 11 346 10 493	-582 335 581 -329 -489	2 82 3 32 4 133 5 63 6 15	-653 313 1336 -627 -124	-3 -2 1 -1	279 - 1207 -1 194 725	531 - 285 - 248 - 141 - 759 -	0 431 8 528 6 1117 4 502 -2 733	-437 535 -1109 553 -743	-1 0 1	43 157 206	490 355 210
8 53 9 80 10 33 11 43 12 27	-801 -291 405	-11 52:	6 -531 -245	-4 2935 -2 1206 0 2240 2 1628 4 2029	2613 -1106 2228 -1602 1991	-14 915 -13 352 -12 246 -11 960 -10 570	-993 -316 -157 -1015 -605	-1 655 0 354 1 462 2 696 3 1050	689 322 -509 -765	-18 39 -16 36 -14 14 -12 83	7 -470 4 410 9 -137 3 967	-8 -7 -0 -5	416 30 522 -52 881 -85 854 85 642 67	-9 1 -8	10 6 282 112	294 -	-8 644 -7 415 -6 757 -5 358 -4 611	615 -401 -809 350 626	8 121 9 43 10 57 11 22	5 1242 7 -451 5 -599 8 199	23456	904 - 293 535 308 - 776 -	904 283 580 303	2 672	-703	-10 -8 -6 -4	36 - 24 89 -	415 96 584 251
13 41 14 25 15 34	-389 -212 240	-9 19 -8 23 -7 19 -6 21 -5 62	68 -259 7 -267 7 -267 7 -883	6 1521 8 1101 10 519 12 861 14 979	-1559 1143 -499 869 -996	-9 550 -8 441 -7 760 -6 1077 -5 170	593 423 -719 -1104 125	4 142 5 256 6 373 7 832 8 271	125 -320 -398 886 283	-10 163 -8 35 -6 338 -4 199 -2 701	1 -1085 8 -230 0 -3148 6 1826 8 -1952	-3 -2 -1 0	615 -69 975 -99 327 29 986 103 441 -40	-7000	315 - 121 300 131 - 326 -	302 -60 311 159 352	-3 486 -2 468 -1 240 0 555 1 496	-496 -478 246 585 -493	-16 40 -14 56 -12 46	0 7 482 6 -618 9 442	7 8 9	269 539 214 -	248 557 - 165 - -	4 266 3 258 12 366 11 240	-293 227 399 -196	ō.	284 22 2 107	295
-17 23 -16 38 -15 25 -14 55	149 340 -163 -552	-4 18 -3 24 -2 17 -1 58 0 24	19 -152 -5 7 595 -149	16 654 4 -17 367	677 2 312	-4 186 -3 1364 -2 242 -1 552 0 669	150 -1256 -243 546 695	9 720 10 401 11 260 12 186	- 741 - 421 253 226	0 123 2 140 4 94 6 71 8 88	1339 2 -1454 6 1015 7 -726 2 888	23450			131 222 142 - 266 - 132	235	2 1038 3 550 4 814 5 796 6 239	-1035 543 848 -769 -234	-10 39 -8 59 -6 39 -4 54 -2 52	-388 5 650 9 -373 0 544 9 -581	-16 -14 -12 -10	208 547 - 450 458 -	185	0 531 9 154 8 192 7 838 6 1255	-517 85 179 -837 -1292	-6 -5 -4 -3	197 - 191 197 -	264 184 190 154
-13 29 -12 73 -11 54	212 735 -469	1 34 2 24 3 35	-362 203 7 366	-15 481 -15 712 -14 1072	-705 -1130	1 482 2 734 3 560	-508 -739 548	-11 189	o -153	12 46	, -993 0 485 4 -471	7 8 9	727 71 215 14	, , ,	140 - 175 -	145	6 610 9 625	649 -633	2 100	-1037 9 1021	-8 -6 -4	695 - 1109 1	-683	-4 214 -3 316	-107 211 -284			

II all the hydrogen atoms except those of the water molecules were located by means of difference maps, while the hydrogen atoms in crystal I were unresolved. Although located in difference maps the hydrogen atoms of crystal II were included in idealized positions. The location of a proton on N(3) in crystal I is inferred from the similarity of the two structures and the necessity of the proton for charge balance. Both structures were initially solved by assuming the molecular formula to be $\frac{1}{2}$ AgNO₂. 10-methylisoalloxazine. 2H₂O, but difference maps calculated without the nitrite ion at late stages of refinement proved the electron density around the 'nitrite' moiety to be significantly different (Fig. 1). In crystal I the insertion of a nitrite ion proved sufficient to describe the density present. On the other hand, a nitrite ion did not offer sufficient electron density to bring $\rho_{obs} - \rho_{calc}$ to a minimum in the region of the nitrite for crystal II. After a number of trials with occupancy and positional parameters varied according to the results of least-squares calculations and difference maps, the final refinement for crystal II was performed with the following occupancy for the nitrite complex: 45% nitrate, 25% nitrite, having its oxygen atoms nearly coincident with the general-position oxygen atoms of the nitrate, and 30% 'disordered' nitrite having the reverse polar sense with respect to the twofold axis.

Final atomic parameters appear in Tables 1 and 2. In the final cycles of least-squares refinement of crystal II, all occupancy parameters were held fixed but heavy atom positions and thermal parameters, except B_{22} of O(2)Nit which tended to negative values, were refined. The function minimized for each structure was $\sum w |F_o - F_c|^2$, with $w = 1/\sigma^2$. Final residuals (R= $\sum |F_o - F_c| / \sum |F_o|$) were 6.2% for structure I and 6.9% for structure II. Observed and calculated structure factors are given in Tables 3 and 4 for crystals I and II respectively. Atomic scattering factors were obtained from International Tables for X-ray Crystallography (1968) except that for hydrogen (Stewart, Davidson & Simpson, 1965) and were corrected for anomalous dispersion (International Tables for X-ray Crystallography, 1968).

Results and discussion

The presence of nitrate and disordered nitrite in crystal II appears to be a result of the peroxide present during crystallization. The addition of peroxide to the system seems to have a dual result: (1) reoxidation of Ag^0 to Ag^+ and (2) reoxidation of NO_2^- to NO_3^- . Formic acid evidently serves as the original reductant and is necessary for significant flavin solubility.

Fig. 1(b) shows both the least-squares and idealized positions for the nitrite complex of crystal II. The idealized angle, 114.9 (5)°, and distance, 1.230 (3) Å, for the nitrite and disordered nitrite are those obtained from neutron diffraction data for the compound NaNO₂ (Kay & Frazier, 1961). The N-O distance of 1.26 (1) Å and the ONO angle of 114 (1)° in crystal I

agree reasonably well with these values. Bond lengths NNit-O(1)Nit = 1.23 (2), NNit-O(1)NitD = 1.25 (5) and NNit-O(2)Nit=1.06 (3) Å were observed for crystal II but are without physical meaning since most atomic sites represent average positions for two or more independent atoms. Idealized nitrite and nitrate groups are shown in Fig. 1 and seem to indicate that the refined positions are physically reasonable. For the idealized nitrate, angles of 120° and a bond length of 1.239 (3) Å, which is the unique N–O distance in the complex hexakis(imidazole)-nickel(II) nitrate (Santoro, Mighell, Zocchi & Reimann, 1969) were assumed. The positions for the idealized nitrate and nitrite ions were fixed so that they best approximated the least-squares refined positions for the entire nitrite complex.



Fig.2. (a) Bond lengths and (b) bond angles. The upper figure of each pair is from crystal II and the lower, crystal I.

The numbering scheme, immediate surroundings of the flavin molecule, and bond distances and angles for both structures are shown in Fig. 2, while the packing



Fig. 3. Flavin π overlap and coordination. The direction of view is perpendicular to the mean flavin plane.

is illustrated in Figs. 3 and 4. These diagrams were made with the parameters of crystal II, but for all practical purposes they are identical with those for crystal I. For simplicity, only the ordered nitrite of the nitrite complex is shown in the diagram. Disregarding the nitrite (nitrate) ions, which must really be regarded as ionic and noncoordinated (see below) the silver ion displays coordination about midway between tetrahedral and square planar. The interplanar angle for the two molecules related by the twofold axis is 40.4° in crystal I and 40.1° in crystal II. The flavin is nearly planar, the folding angle between 8-atom planes through the benzenoid and pyrimidinoid portions of the flavin moiety having N(5) and N(10) in common (Table 5) being 2.0° for crystal I and 3.8° for crystal II. Table 5 also shows a slight twist along the long axis of the flavin molecule as is seen in 10-methylisoalloxazine silver nitrate (Fritchie, 1972a).

The Ag-N bond distances at the primary chelate site N(5) and O(4) are 2.294 (6) Å in 10-methylisoalloxazine silver nitrate (Fritchie, 1972*a*), 2.295 (5) Å in riboflavin silver perchlorate hemihydrate (Wade & Fritchie, 1973), 2.25 (2) Å and 2.40 (2) Å in bis-(10methylisoalloxazine)sesqui(silver perchlorate) (Sproul

Table 5. Deviations of the isoalloxazine moieties from planarity

All atoms are given equal weights. The distances given in parentheses indicate atoms not used in calculating the planes. The planes are expressed as Am + Bn + Cp = D where m, n, and p are dimensions in Å relative to unit orthogonal axes $m || \mathbf{b} \times \mathbf{c}^*, n || \mathbf{b}$, and $p || \mathbf{c}^*$. Planes I, II, and II represent planes through the entire flavin, the benzenoid and pyrimidinoid moieties of crystal I respectively while planes IV, V, and VI follow the same sequence for crystal 2.

	Coefficients		_	-	_	
	Plane	A	В	С	D	
	I	0.27023	<i>−</i> 0·93846	-0.21209	4.227	
	II	0.22576	- 0.94740	-0.22688	3.244	
	III	0.31235	- 0 ·92658	-0·20951	4·994	
	IV	0.27494	-0.39391	-0.20639	4.290	
	v	0.24433	-0.94305	-0.22577	3.636	
	VI	0.30856	-0.93127	-0.19372	4.921	
Distances fro	m planes					
	(I)	(II)	(III)	(IV)	(V)	(VII)
Ag	(0·554) Å	(0·581) Å	(0·670) Å	(0·152) Å	(0·118) Å	(0·281) Å
OW(1)	(0.526)	(0.850)	(0.402)	(0.590)	(0.836)	(0.465)
N(1)	0.040	(0.254)	0.008	0.02	(0.199)	0.018
C(2)	0.102	(0.352)	0.028	0.116	(0.278)	0.024
O(2)	(0.218)	(0.525)	(0.091)	(0.193)	(0.397)	(0.086)
N(3)	0.020	(0.297)	0.010	0.011	(0.139)	-0.027
C(4)	-0.053	(0.113)	-0.057	-0.054	(0.027)	-0.041
O(4)	(-0.152)	(-0.008)	(-0.144)	(-0.180)	(-0.126)	(-0.148)
C(4a)	-0.053	(0.069)	-0.010	<i>−</i> 0·052)	(0.012)	-0.010
N(5)	-0.042	0.017	0.052	-0.030	-0.010	0.062
C(5a)	-0.042	-0.023	(0.093)	- 0.006	-0.005	(0.112)
C(6)	0.044	0.003	(0.244)	0.020	0.002	(0.222)
C(7)	0.083	0.003	(0.325)	0.067	0.002	(0.267)
C(8)	0.067	0.010	(0.296)	0.030	0.003	(0.205)
C(9)	-0.004	0.006	(0.165)	-0.040	-0.050	(0.084)
C(9a)	-0.085	(-0.033)	(0.045)	-0.029	0.008	(0.066)
N(10)	-0.092	0.018	-0.028	-0.074	(0.011)	-0.031
C(10)	(-0.140)	(0.001)	(−0·091)	(-0.109)	(0.011)	(-0.092)
C(10a)	-0.026	(0.126)	-0.003	-0.040	(0.060)	-0.025
OW(2)	(0.419)	(0.725)	(0.270)	(0.380)	(0.541)	(0.286)
N Nit	(0.196)	(0.689)	(-0.083)	(0.416)	(0.792)	(0.149)
O(1)Nit	(1.054)	(1.496)	(0.802)	(1.322)	(1.666)	(1.084)
O(2)Nit				(-0.583)	(-0.212)	(-0.842)
O(1)NitI	2			(-0.073)	(0.268)	(-0.299)

& Fritchie, 1973) (the latter Ag–N bond is not strictly comparable owing to silver six coordination instead of the square planar or tetrahedral four coordination in all other cases), and 2.373 (9) and 2.303 (6) Å for crystals I and II respectively. These distances are not much longer than those found in the complex bis-(8hydroxyquinoline)-silver(I) pyridine solvate (Fleming & Lynton, 1968), 2.145 and 2.155 (4) Å, a bond which probably has considerable covalent character. However, the large difference in Ag–N(5) distance in crystals I and II suggests that the Ag–N(5) bond strength does not vary rapidly with distance as would be expected if a redox-active silver atom were donating charge into the flavin nucleus by a back-bonding mechanism.

A detailed analysis of the geometries of oxidized (Norrestam & Stensland, 1972), reduced (Norrestam, von Glehn, Wagman & Kierkegaard, 1969), and the above silver-containing (Fritchie, 1972*a*; Wade & Fritchie, 1973) flavin compounds as shown in Table 6 and Fig. 2(a) leads to the conclusion that the silver compounds are more similar to the oxidized moiety than to the semiquinone, the latter assumed to be the average of oxidized and reduced flavins. Indeed, the N(1)-C(10a), C(4a)-N(5) and C(4a)-C(10a) diagnostic bonds (Fritchie, 1972a) agree well with those in the oxidized form of the flavin ligand. In agreement with these results, Lauterwein, Hemmerich & Lhoste (1972) have recently reported, on the basis of n.m.r. contact and pseudo-contact shifts, that quinoid flavin com-



Fig. 4. [010] projection. Hydrogen bonds and bonds to Ag⁺ are dashed.

Tal	ole	6.	Bond	lengths	in	oxidized,	, reduced	, and	Ag c	helated	flavins
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	Oxidized	Reduced	Chela	ted
	Ι	11	III	IV
N(1)C(10a)	1·317 (4) Å	1·391 (8) Å	1·321 (10) Å	1·323 (7) Å
C(10a) - C(4a)	1.452 (5)	1.350 (8)	1.406 (12)	1.442 (8)
C(4a) - N(5)	1.302 (4)	1.385 (8)	1.288 (10)	1.309 (7)
N(1) - C(2)	1.363 (5)	1.367 (8)	1.386 (10)	1.363 (8)
C(2)O(2)	1.217 (5)	1.193 (8)	1.222 (10)	1.249 (8)
C(2) - N(3)	1.410 (5)	1.391 (8)	1.398 (12)	1.368 (8)
N(3)C(4)	1.355 (4)	1.380 (8)	1.370 (10)	1.347 (8)
C(4)O(4)	1.220 (5)	1.223 (8)	1.212 (11)	1.221 (7)
C(4) - C(4a)	1.477 (5)	1.432 (8)	1.500 (11)	1.464 (9)
N(5) - C(5a)	1.366 (5)	1.394 (8)	1.390 (10)	1-351 (8)
C(5a) - C(9a)	1.410 (5)	1.404 (8)	1.392 (12)	1.408 (8)
C(9a) - N(10)	1.381 (4)	1.438 (8)	1.409 (10)	1.402 (7)
N(10) - C(10a)	1.365 (5)	1.386 (8)	1.366 (10)	1.357 (7)
Ag(1) - N(5)		• •	2.294 (6)	2.295(5)
Ag(1) - O(4)			2.484 (6)	2.521(5)
Ag(2) - N(1)			2.827 (6)	2.304 (5)
Ag(2) - O(2)			2.629 (6)	2.786 (5)

I=Average values for: 3-methyllumiflavin (Norrestam & Stensland, 1972), 10-methylisoalloxazine (Wang & Fritchie, 1973), lumiflavin bis(naphthalene-2,3-diol) (Wells, Trus, Johnston, Marsh & Fritchie, 1972); II=9-bromo-5-hydro-1,3,7,8,10-penta-methyl-1,5-dihydro-alloxazine (Norrestam, Glehn, Hagman & Kierkegaard, 1969); III=10-methylisoalloxazine silver nitrate (Fitchie, 1972a); IV=riboflavin silver perchlorate hemihydrate (Wade & Fritchie, 1973).

Table 7. Visible and i	ultraviol	et s	pectra
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10MeISO†- H₂O	10MeISO-solid	Riboflavin	Sodium salt of FMN	1(10-MeISO)- <u> 1</u> AgNO ₂ -2H ₂ O	2(10Me-ISO)- 3AgClO₄
435 nm (23·0)‡	500 nm (20·0) 464 nm (shoulder) (21·6) 430 nm (shoulder) (23·3)	505 nm (19·8) 475 nm (21·1)	505 nm (19·8) 475 nm (21·1)	525 nm (19·0) 492 nm (shoulder) (20·3)	515 nm (19·4) 470 nm (shoulder) (21·3)
340 nm (29·4) 280 nm (35·7) 215 nm (46·5)	370 nm (27·0) 290 nm (34·5) 220 nm (45·5)	390 nm (25·6) 295 nm (33·9) 230 nm (43·5)	395 nm (25·3) 295 nm (33·9) 230 nm (43·5)	377 nm (26·5) 292 nm (34·2) 222 nm (45·0)	380 nm (26·3) 290 nm (34·5) 225 nm (44·4)

* Peak positions of four main regions of absorption.

† 10MeISO refers to 10-methylisoalloxazine.

‡ Numbers in parentheses refer to energies in kilokaysers.

plexes with a number of metals including Ag⁺ and Cu²⁺ involve primarily σ rather than π interactions.

Although bond geometries of the silver-containing flavin compounds tend to argue against significant charge-transfer interaction between silver and the π electron system of the flavin in the ground state, spectroscopic evidence (Table 7) demonstrates significant perturbation of the π -electron system. Part of the longwavelength shift of the flavin bands in comparison with the solution spectrum is a commonly observed solid-state effect (Wolf, 1959), but the further shift in the silver complexes must be due to coordination. Both the structural and the spectroscopic results can be rationalized if one assumes that there is little chargetransfer stabilization of the ground state and that the first excited states actually involve flavin \rightarrow metal charge transfer rather than the reverse. Mixing with empty, not filled metal orbitals, is required to stabilize empty orbitals on the flavin and this is the most likely explanation for the shift of the 370 and 500 nm bands to lower energies in the silver complexes. The out-ofplane 5p orbital of Ag⁺ is suitable for this purpose. That these energy changes are not due totally to simple solid state stabilization or $\pi - \pi$ interaction is shown by the fact that they are greater in the silver complexes where flavin-flavin π interaction is less (3.31 Å in crystal I and 3.33 Å in crystal II) than in simple 10methylisoalloxazine, where the π separation is smaller (3.25 Å) and hence possible flavin-flavin interaction greater.

The extent of the shift in the longest wavelength band in the silver-flavin complexes does not correlate, however, with Ag-N distances. The Ag-N(5) distance in this structure [2.373 (7) Å] is greater than in the perchlorate complex [2.25 (2) Å] while at the same time the longest wavelength absorption band shows a greater shift in this structure. The primary chelate site rather than the secondary site is presumed to be spectroscopically more important owing to large participation of N(5) and very small participation of N(1) in the lowest empty molecular orbital, as shown by electron spin resonance measurements on the semiguinone (Ehrenberg, Eriksson & Hemmerich, 1965). The greater shift in this structure is in agreement with the argument that stabilization may be due to 5p silver orbitals, since in this quasi-tetrahedral structure there would be much less competition of the two flavin molecules for the same p orbital than in the nearly planar perchlorate complex.

Unlike the previous silver-flavin complexes reported, only one silver ion is found per two flavin molecules. Consequently, the stability of this silver-flavin complex cannot be attributed entirely to that gained from a polymeric structure built up by alternation of silver ions and flavin molecules. Indeed the distances for N(1)-OW(1) and O(2)-OW(1), 3.14 (2) and 3.04 (2) for crystal I and 3.10 (2) and 3.10 (2) Å for crystal II, are rather long to be associated with strong hydrogen bonding, indicating somewhat weak intermolecular

interactions. Closer examination of the packing in these structures reveals a variety of interactions holding the molecular structure together. As Figs. 3 and 4 reveal, van der Waals interactions are the most important binding forces in the **b** direction. Fig. 3 shows the overlap of two of these molecules; a third molecule related to one of the first two by a twofold axis through the silver atom is also shown. The interplanar spacing, based on the least-squares plane through all 17 atoms, is 3.31 Å for crystal I and 3.33 Å for crystal II.

From Fig. 4 it is evident that hydrogen bonding is the greatest stabilizing force in the c direction. Table 8 lists the possible hydrogen bonds. A reasonable scheme for proton positions would have the protons of OW(1)being donated to either N(1) or O(2) and to the nitrite complex; the N(3) proton donated to OW(2); and a proton of OW(2) donated to an OW(1) molecule related by a c glide.

Table 8. Possible hydrogen bonds

	Crystal I	Crystal II
N(3) = OW(2)	2·84 (2) Å	2·87 (1) Å
N(1) - OW(1)	3.14(2)	3.10 (2)
O(2) - OW(1)	3.04 (2)	3.10(1)
OW(1) - O(1)Nit	2.77 (2)	3.11 (2)
OW(1) - O(1)NitD		2.78 (2)
$OW(1)^* - OW(2)$	2.84 (2)	2.77 (2)

* Transformed by symmetry to $(x, -y, \frac{1}{2} + z)$.

The existence in crystal II of both an 'ordered' nitrite site (analogous to that in crystal I) and a 'disordered' site may be connected with the following changes in the structure. In crystal I, the single nitrite can both coordinate moderately strongly to Ag^+ [$O \cdots Ag^+ =$ 2.74 (2) Å] and hydrogen-bond to water OW(1)[$O \cdots O = 2.77$ (2) Å], whereas in crystal II the ordered nitrite, which remains fairly strongly coordinated to

Table 9. Closest intermolecular approach distances

Superscripts designate symmetry transformations as follows:

$i \frac{\frac{3}{2} - x}{ii} \frac{\frac{1}{2} + x}{\frac{1}{2} + x}$ $iii \frac{1}{2} + x$	$\begin{array}{cccc} \frac{1}{2} - y & -z \\ \frac{1}{2} + y & z \\ \frac{1}{2} - y & \frac{1}{2} + z \end{array}$	
	Crystal II	Crystal I
$N(1) \cdots O(2^i)$	3·21 (2) Å	3·22 (4) Å
$N(1) \cdots O(2^{i})$	3.37(2)	3.39 (4)
$H(8) \cdots N^{ii} Nit$	3.20	
$H(9) \cdots N^{ii}Nit$	2.76	
$H(8) \cdots O(1^{ii})$ Nit	2.77	
$H(9) \cdots O(1^{ii})$ Nit	3.01	
$H(9) \cdots O(2^{ii})$ Nit	3.22	
$H(8) \cdots O(1^{ii}) NitD$	3.23	
$H(7) \cdots O(2^{11})$	2.58	
$H(8) \cdots O(2^{ii})$	2.70	
$H(6) \cdots OW(2^{ii})$	3.24	
$H(7) \cdots OW(2^{ii})$	2.53	
$H(6) \cdots O(2^{ii})$ Nit	3.08	
$H(6) \cdots O(1^{iii})$ NitD	2.82	

Ag⁺ [O···Ag⁺ = 2.75 (2) Å], is much farther from OW(1) [O···O = 3.11 (2) Å]. The alternate, 'disordered' site provides a stronger hydrogen bond [2.78 (2) Å] at the expense of lost Ag⁺ coordination [O(1)NitD is 3.18 (2) Å from the silver on the opposite side of NNit]. At the same time, because each nitrite ion lies between two silver ions on the twofold axis, there is presumably no great change in coulombic stabilization of the crystal. The distance from the second silver ion to O(2)NIT of the nitrate group in crystal II is 2.70 (2) Å.

Other than the contacts discussed above, there are no unusually short distances in the structure. Table 9 lists the shortest remaining van der Waals contacts.

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The Crystal Structures of R₂Co₁₇ Intermetallic Compounds

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The R_2Co_{17} intermetallic compounds are known to crystallize in two polymorphic forms, a hexagonal of the Th_2Ni_{17} -type structure and a rhombohedral of the Th_2Zn_{17} -type structure. The crystal structure of a new high-temperature disordered phase of R_2Co_{17} is given. The two above-mentioned crystal modifications of R_2Co_{17} are shown to be the superstructures of this disordered phase. The stability of the new phase and the conditions for its transformation into its super-structures are given. The degree of order of R_2Co_{17} of the Th_2Ni_{17} -type structure is discussed.

Introduction

The R_2Co_{17} intermetallic compounds (R = rare earths including Y) exhibit polymorphism (Ostertag & Strnat, 1965; Buschow, 1966; Lemaire, 1966). Most of them

have been reported to crystallize in two modifications, a high-temperature phase of the Th_2Ni_{17} -type structure and a low-temperature phase of the Th_2Zn_{17} -type structure (Bouchet, Laforest, Lemaire & Schweizer, 1966). However, it has been recently reported that the