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 $a = 21 \cdot 764$ (11), $b = 7 \cdot 005$ (4), $c = 17 \cdot 336$ (9) Å, $\beta = 107 \cdot 57$ (2)°, $Z = 8$, $\mu = 60 \cdot 9$ cm^{-1}, $\varrho_{obs} = 1 \cdot 83$, and $\varrho_{calc} = 1 \cdot 80$ g cm^{-3} with molecular formula $\frac{1}{2}AgNO_2 \cdot C_{11}H_8N_4O_2 \cdot 2H_2O$. The final R for structure I, based on 588 counter-measured reflections, is $6 \cdot 2\%$. Crystal II with molecular formula $\frac{1}{2}Ag(NO_2)_{0 \cdot 55}(NO_3)_{0 \cdot 45} \cdot C_{11}H_8N_4O_2 \cdot 2H_2O$ has cell constants $a = 21 \cdot 732$ (5), $b = 7 \cdot 092$ (2), $c = 17 \cdot 503$ (4) Å, $\beta = 107 \cdot 63$ (1)°, $Z = 8$, $\mu = 59 \cdot 5$ cm^{-1}, $\varrho_{obs} = 1 \cdot 80$ and $\varrho_{calc} = 1 \cdot 78$ g cm^{-3}. The final R, based on 1561 counter-measured reflections, is $6 \cdot 9\%$. 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 [$2 \cdot 600$ (9) Å in I and $2 \cdot 612$ (7) Å in II] but Ag$^+$–N values differ [$2 \cdot 373$ (9) Å in I and $2 \cdot 303$ (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 $40 \cdot 4°$ in crystal I and $40 \cdot 1°$ in crystal II.

Introduction

Flavoproteins form an important class of oxidation-reduction 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 co-workers (Hemmerich & Spence, 1966; Hemmerich, Müller & Ehrenberg, 1965; Bamberg & Hemmerich, 1961) have shown that flavin in its semiquinone 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 semiquinone formation. These workers have interpreted the selective metal affinity of quinoid flavin in terms of metal →

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, 1972*a*; Wade & Fritchie, 1973) and of a Cu(II) complex (Fritchie, 1972*b*) 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 → 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 $K\alpha$ 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 $K\alpha$ 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 $\frac{1}{2}AgNO_2 . C_{11}H_8N_4O_2 . 2H_2O$, 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 $\frac{1}{2}Ag(NO_2)_{0.55}(NO_3)_{0.45} . C_{11}H_8N_4O_2 . C_{11}H O_2 . 2H_2O$, 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 = 38·20, H = 3·51, N = 18·28%; composition calculated for $\frac{1}{2}AgNO_2 . C_{11}H_8N_4O_2 . 2H_2O$: C = 38·71, H = 3·52, N = 18·47%; for $\frac{1}{2}Ag(NO_2)_{0.55}(NO_3)_{0.45} . C_{11}H_8N_4O_2 . 2H_2O$: C = 38·26, H = 3·48, N = 18·26%).

Intensities were measured with Cu $K\alpha$ radiation to a limit of $2\theta = 70°$ for crystal I and $2\theta = 112°$ 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(Tl)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-

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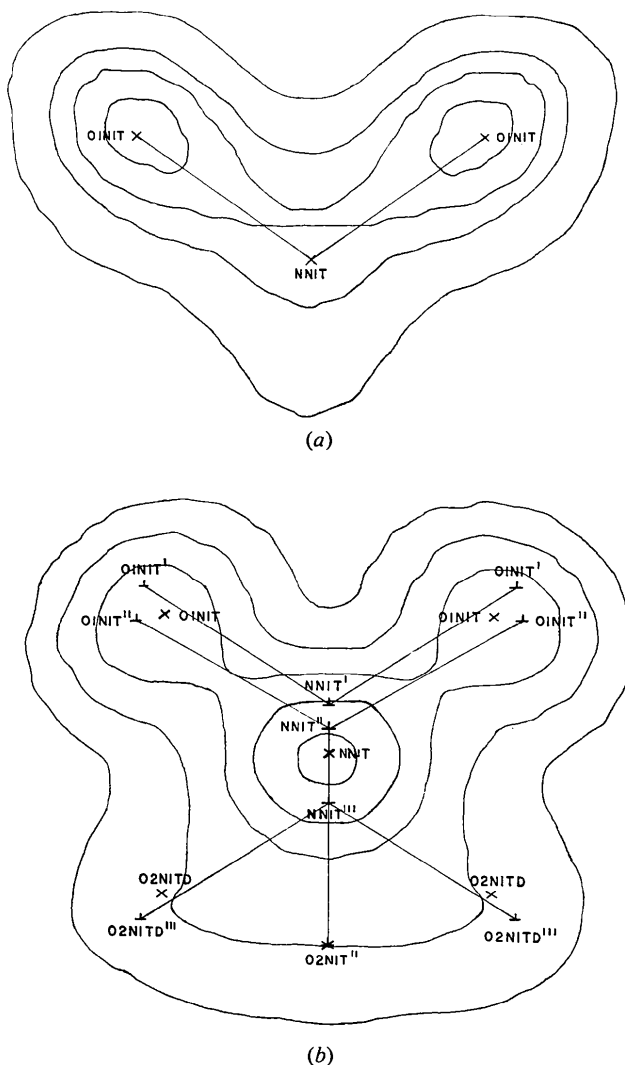

(a)

(b)

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.

Table 1. *Positional and isotropic thermal parameters*

The first entry of each pair corresponds to crystal I, the second to crystal II. The entries for hydrogen atoms correspond to crystal II only.

Atom	x	y	z	B
Ag	1·0*	−0·0217 (2)	¼*	
	1·0*	0·0435 (2)	¼*	
OW(1)	0·6737 (9)	0·0187 (18)	−0·1840 (9)	
	0·6803 (8)	0·0122 (18)	−0·1859 (7)	
OW(2)	0·7217 (4)	−0·2143 (17)	0·2026 (6)	
	0·7217 (3)	−0·2037 (15)	0·2011 (4)	
NNit	¼*	−0·0366 (40)	¼*	
	¼*	−0·0758 (18)	¼*	
O(1)Nit†	0·5509 (5)	−0·1347 (23)	−0·2310 (7)	
	0·5463 (8)	−0·1851 (20)	−0·2298 (8)	
O(2)Nit‡	$\bar{\tfrac{1}{4}}$*	0·0742 (34)	$\bar{\tfrac{1}{4}}$*	
O(1)NitD§	0·5466 (21)	0·0338 (75)	−0·2425 (3)	
N(1)	0·7896 (5)	0·0771 (17)	−0·0246 (6)	1·8 (2)
	0·7902 (3)	0·0743 (11)	−0·0268 (4)	
C(2)	0·7589 (8)	−0·0025 (17)	0·0236 (10)	2·4 (4)
	0·7575 (4)	−0·0009 (11)	0·0226 (5)	
O(2)	0·7012 (5)	−0·0462 (13)	−0·0035 (6)	3·1 (2)
	0·7006 (3)	−0·0435 (11)	−0·0043 (4)	
N(3)	0·7876 (6)	−0·0288 (14)	0·1054 (7)	1·9 (3)
	0·7883 (3)	−0·0173 (11)	0·1039 (4)	
C(4)	0·8500 (7)	0·0170 (17)	0·1432 (9)	1·8 (4)
	0·8507 (4)	0·0209 (12)	0·1411 (5)	
O(4)	0·8755 (5)	−0·0012 (11)	0·2176 (7)	2·9 (3)
	0·8748 (3)	0·0085 (11)	0·2130 (6)	
C(4a)	0·8877 (6)	0·0897 (20)	0·0918 (8)	1·4 (3)
	0·8873 (4)	0·0930 (11)	0·0873 (5)	
N(5)	0·9486 (4)	0·1199 (15)	0·1225 (6)	1·4 (2)
	0·9487 (3)	0·1216 (10)	0·1183 (4)	
C(5a)	0·9819 (5)	0·1895 (17)	0·0701 (7)	1·0 (3)
	0·9820 (3)	0·1841 (11)	0·0691 (5)	
C(6)	1·0492 (6)	0·2111 (19)	0·1027 (8)	1·7 (3)
	1·0491 (4)	0·2133 (14)	0·0993 (5)	
C(7)	1·0834 (5)	0·2723 (18)	0·0544 (7)	1·3 (3)
	1·0845 (4)	0·2781 (14)	0·0509 (6)	
C(8)	1·0537 (6)	0·3099 (19)	−0·0273 (8)	2·1 (3)
	1·0513 (4)	0·2142 (12)	−0·0312 (5)	
C(9)	0·9855 (6)	0·2873 (19)	−0·0639 (7)	1·7 (3)
	0·9868 (4)	0·2900 (13)	−0·0623 (5)	
C(9a)	0·9515 (5)	0·2275 (17)	−0·0107 (7)	0·8 (3)
	0·9508 (3)	0·2194 (11)	−0·0125 (4)	
C(10a)	0·8521 (6)	0·1174 (20)	0·0076 (7)	1·5 (3)
	0·8518 (3)	0·1204 (13)	0·0043 (5)	
N(10)	0·8860 (4)	0·1938 (14)	−0·0395 (6)	1·1 (2)
	0·8850 (2)	0·1900 (11)	−0·0431 (4)	
C(10)	0·8503 (6)	0·2364 (20)	−0·1291 (8)	2·1 (3)
	0·8509 (4)	0·2262 (17)	−0·1267 (5)	
H(3)	0·7629	−0·0577	0·1365	3·0
H(6)	1·0698	0·1894	0·1539	3·0
H(7)	1·1293	0·2984	0·0715	3·0
H(8)	1·0753	0·3574	−0·0652	3·0
H(9)	0·9658	0·3173	−0·1170	3·0
H(1)CH₃	0·8643	0·1403	−0·1612	3·0
H(2)CH₃	0·8618	0·3524	−0·1431	3·0
H(3)CH₃	0·8045	0·2235	−0·1364	3·0

* These parameters are fixed by symmetry.
† Population factor is 0·45 (nitrate) and 0·25 (nitrite).
‡ Population factor is 0·45.
§ Population factor is 0·30.

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 $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.
For atoms Ag through O(1)Nit the first entry corresponds to crystal I, the second to crystal II as in Table 1
Entries from O(2)Nit to C(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*
	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 (11)	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.

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 op-

portunity 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*, $10|F_o|$ and $10F_c$, and is headed by the values of *h* and *k* common to the group.

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 $\frac{1}{2}$AgNO$_2$.10-methylisoalloxazine.2H$_2$O, 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 $\varrho_{obs} - \varrho_{calc}$ 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.
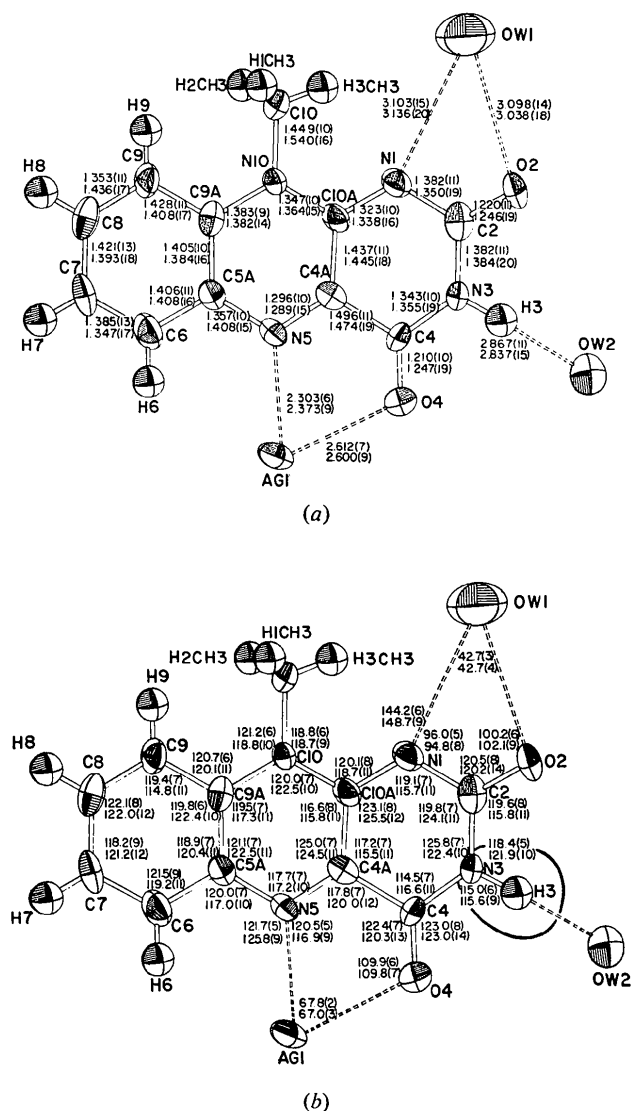
Final atomic parameters appear in Tables 1 and 2. In the final cycles of least-squares refinement of crystal II, all occupancy parameters were held fixed but heavy atom positions and thermal parameters, except B_{22} of O(2)Nit which tended to negative values, were refined. The function minimized for 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 NaNO$_2$ (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.

(a)

(b)

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
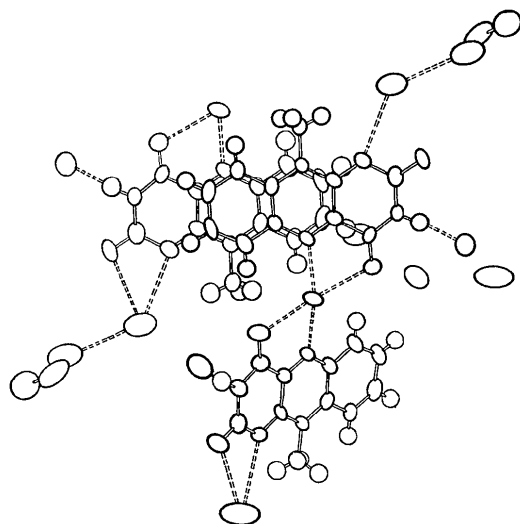

Fig. 3. Flavin π overlap and coordination. The direction of view is perpendicular to the mean flavin plane.

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, 1972a), 2·295 (5) Å in riboflavin silver perchlorate hemihydrate (Wade & Fritchie, 1973), 2·25 (2) Å and 2·40 (2) Å in bis-(10-methylisoalloxazine)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 $m \| b \times c^*$, $n \| b$, and $p \| c^*$. 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	B	C	D
I	0·27023	−0·93846	−0·21509	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 from 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	0·052	(0·199)	0·018
C(2)	0·102	(0·352)	0·028	0·116	(0·278)	0·054
O(2)	(0·218)	(0·525)	(0·091)	(0·193)	(0·397)	(0·086)
N(3)	0·070	(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	−0·052)	(0·012)	−0·010
N(5)	−0·045	0·017	0·052	−0·030	−0·010	0·062
C(5a)	−0·047	−0·023	(0·093)	−0·006	−0·002	(0·112)
C(6)	0·044	0·003	(0·244)	0·050	0·005	(0·222)
C(7)	0·083	0·003	(0·325)	0·067	0·005	(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	−0·020	(0·084)
C(9a)	−0·082	(−0·033)	(0·045)	−0·029	0·008	(0·066)
N(10)	−0·095	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)NitD				(−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 lo¬ger than those found in the complex bis-(8-hydroxyquinoline)–silver(I) pyridine solvate (Fleming & Lynton, 1968), 2·145 and 2·155 (4) Å, a bond which probabl/ 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, 1972a; 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-
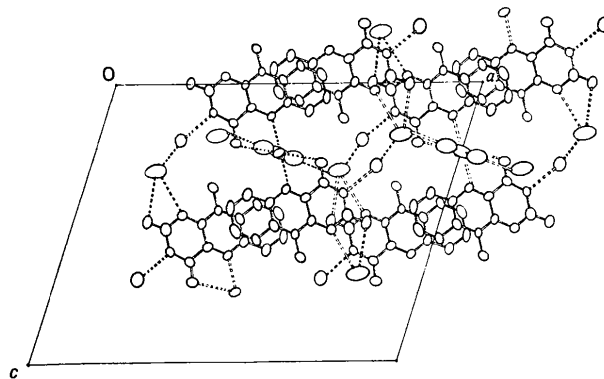

Fig. 4. [010] projection. Hydrogen bonds and bonds to Ag^+ are dashed.

Table 6. *Bond lengths in oxidized, reduced, and Ag chelated flavins*

	Oxidized I	Reduced II	Chelated III	Chelated 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-pentamethyl-1,5-dihydro-alloxazine (Norrestam, Glehn, Hagman & Kierkegaard, 1969); III = 10-methylisoalloxazine silver nitrate (Fritchie, 1972a); IV = riboflavin silver perchlorate hemihydrate (Wade & Fritchie, 1973).

Table 7. *Visible and ultraviolet spectra**

10MeISO†–H$_2$O	10MeISO-solid	Riboflavin	Sodium salt of FMN	1(10–MeISO)–½AgNO$_2$–2H$_2$O	2(10Me–ISO)–½AgClO$_4$
435 nm (23·0)‡	500 nm (20·0)	505 nm (19·8)	505 nm (19·8)	525 nm (19·0)	515 nm (19·4)
	464 nm (shoulder) (21·6)	475 nm (21·1)	475 nm (21·1)	492 nm (shoulder) (20·3)	470 nm (shoulder) (21·3)
	430 nm (shoulder) (23·3)				
340 nm (29·4)	370 nm (27·0)	390 nm (25·6)	395 nm (25·3)	377 nm (26·5)	380 nm (26·3)
280 nm (35·7)	290 nm (34·5)	295 nm (33·9)	295 nm (33·9)	292 nm (34·2)	290 nm (34·5)
215 nm (46·5)	220 nm (45·5)	230 nm (43·5)	230 nm (43·5)	222 nm (45·0)	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 Cu^{2+} 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 long-wavelength 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 charge-transfer 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-of-plane $5p$ orbital of Ag$^+$ is suitable for this purpose. That these energy changes are not due totally to simple solid state stabilization or π–π 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 10-methylisoalloxazine, 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 semiquinone (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	$\frac{3}{2}-x$	$\frac{1}{2}-y$	$-z$
ii	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
iii	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$

	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^{ii})	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^{iii})Nit	3·08	
H(6)$\cdots$O(1^{iii})NitD	2·82	

Ag$^+$ [O$\cdots$Ag$^+$ = 2·75 (2) Å], is much farther from OW(1) [O$\cdots$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 R$_2$Co$_{17}$ Intermetallic Compounds

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The R$_2$Co$_{17}$ intermetallic compounds are known to crystallize in two polymorphic forms, a hexagonal of the Th$_2$Ni$_{17}$-type structure and a rhombohedral of the Th$_2$Zn$_{17}$-type structure. The crystal structure of a new high-temperature disordered phase of R$_2$Co$_{17}$ is given. The two above-mentioned crystal modifications of R$_2$Co$_{17}$ 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$_2$Co$_{17}$ of the Th$_2$Ni$_{17}$-type structure is discussed.

Introduction

The R$_2$Co$_{17}$ 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$_2$Ni$_{17}$-type structure and a low-temperature phase of the Th$_2$Zn$_{17}$-type structure (Bouchet, Laforest, Lemaire & Schweizer, 1966). However, it has been recently reported that the