MORIMOTO, N., GREIG, J. W. & TUNELL, G. (1960). *Carnegie Inst. Wash. Year Book*, **59**, 122.

MORIMOTO, N. & KULLERUD, G. (1961). *Amer. Min.* **46**, 1270.

MORIMOTO, N., MARUMO, F. & SADANAGA, R. (1962). *Amer. Min.* **47**, 197 (Abstract).

PAULING, L. & BROCKWAY, L. O. (1932). *Z. Kristallogr.* **82**, 188.

STROCK, L. W. (1934). *Z. Phys. Chem.* B, **25**, 441.

STROCK, L. W. (1935). *Z. Phys. Chem.* B, **31**, 132.

TUNELL, G. & ADAMS, C. E. (1949). *Amer. Min.* **34**, 824.

VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.

ZIES, E. G. & MERWIN, H. E. (1955). *Amer. Min.* **40**, 1001.

The Structure of Coordination Compounds I. The Crystal and Molecular Structure of Azidopentamminecobalt(III) Azide

BY GUS J. PALENIK

*Chemistry Division, Research Department, U.S. Naval Ordnance Test Station, China Lake, California, U.S.A.*

Azidopentamminecobalt(III) azide, $[N_3Co(NH_3)_5](N_3)_2$, forms dark red prismatic crystals, with space group *Pnam* and unit cell dimensions

$$a = 12 \cdot 997 \pm 0 \cdot 005, \quad b = 8 \cdot 031 \pm 0 \cdot 004, \quad c = 10 \cdot 414 \pm 0 \cdot 004 \text{ Å}.$$

With four molecules per unit cell, the cation is required to have symmetry *m*. The azido group in the coordination sphere is asymmetric with N–N distances of $1 \cdot 145$ and $1 \cdot 208$ Å. The angle Co–N–N is $124 \cdot 8°$. The azide anion is symmetric and linear with N–N distances of $1 \cdot 158$ and $1 \cdot 172$ Å. The final value of the residual R was $7 \cdot 5\%$ for all the 1412 observed reflections.

Introduction

A survey of the literature revealed relatively few three-dimensional structure determinations of coordination compounds. Of the three-dimensional studies reported, a smaller number were concerned with a systematic study of the bonding in coordination compounds. We have decided to investigate the structures of a series of ammine complexes of cobalt and chromium to obtain structural information on these complexes. The following represents a report of the first structural investigations in the proposed study, azidopentamminecobalt(III) azide,

$$[N_3Co(NH_3)_5](N_3)_2 .$$
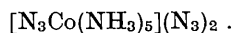
The bonding of the azido group in coordination compounds has been the subject of some speculation. Linhard, Siebert & Weigel (1958) concluded that the greater shift to the red in the infrared spectra of azidopentamminecobalt salts indicated stronger metal-to-nitrogen bonding compared with the chromium complexes. Linhard & Berthold (1958) speculated that the lower impact sensitivity of azidopentamminechromium(III) salts resulted from the more polar character of the chromium–azide bond. Fujita, Nakamota & Kobayashi (1956), however, concluded from a study of the N–N stretching frequencies in the infrared that the cobalt–nitrogen bond in coordinated azides was more ionic than the corresponding chromium–nitrogen bond. The increased ionic character was used to explain the ease of aquation of the cobalt(III) azide complex compared with the chromium(III) complexes. On the basis of infrared spectra of various azide complexes of cobalt(III), Staples & Tobe (1960) considered the azide group to be unsymmetrical and linear with the Co–N–N angle between 108 and 120°.

An X-ray crystal structure determination of azidopentamminecobalt(III) azide was undertaken to resolve the question of the bonding of the azido group in coordination compounds. The azide was chosen since it permits a comparison of both anionic and coordinated azides in the same structure determination.

Experimental

Azidopentamminecobalt(III) azide forms dark red prismatic crystals. Rotation and Weissenberg photographs were taken with two different crystals, one with **a** and one with **b** as the rotation axis. The systematic absences observed on the Weissenberg photographs were:

$0kl$ if $k+l=2n+1$

$h0l$ if $h =2n+1$

$hk0$ no absences

hkl no absences

The most probable space groups are $Pnam$ (D_{2h}^{16}) or $Pna2_1$ (C_{2v}^9).

Cell constants were measured with a single-crystal orienter and molybdenum radiation $(\alpha_1 = 0.70926$ Å and $\alpha_2 = 0.71354$ Å). The following values were obtained:

$$a = 12.997 \pm 0.005, \quad b = 8.031 \pm 0.004,$$
$$c = 10.414 \pm 0.004 \text{ Å}.$$

The density determined by flotation in a carbon tetrachloride–methylene iodide solution was 1.654 g.cm^{-3}, corresponding to 4.01 molecules per unit cell. The density calculated for four molecules is 1.650 g.cm^{-3}.

A small crystal, $0.16 \times 0.13 \times 0.13$ mm, was used to collect the three-dimensional data. A total of 1683 reflections with $2\theta \le 60.0°$ was measured with a proportional counter, molybdenum radiation and the stationary crystal–stationary counter technique being used. Various zirconium filters were used to moderate the counting rate to less than 1000 counts per second and to reduce the β-radiation contribution to the intensity. All reflections were measured by the time required to reach a fixed number of counts. The total number of counts for each reflection was chosen so that the time required was a minimum of about 12 seconds and a maximum of about 100 seconds. Reflections with an intensity less than 10 counts per second were therefore counted only up to a total of 400 counts. The filter factors were determined experimentally. Background corrections were made by measuring the background at various points in the portion of reciprocal space which was studied and by averaging the values obtained at a given 2θ setting. The $\alpha_1 - \alpha_2$ splitting correction was determined by slowly scanning various reflections and comparing the values with the corresponding values obtained from the stationary crystal method. The data were scaled by counting the 200 reflection at the beginning and end of each session of intensity measurements and averaging the values. The raw intensity data were processed by an IBM 709 computer to make the various corrections for background, filter factors, etc., yielding a set of observed structure amplitudes.

Determination and refinement of the structure

A sharpened three-dimensional Patterson synthesis with the origin peak removed was calculated. The positions of the cobalt, the five ammine groups, and the azide group in the coordination sphere were easily located. Since the cobalt atom, the three ammines and the azido group were located in the same plane, the most probable space group appeared to be $Pnam$. The structure analysis was continued on the assumption that $Pnam$ was the most probable space group.

A three-dimensional Fourier synthesis was computed from all the observed reflections using phases calculated on the basis of the cobalt and seven of the ten independent nitrogen atoms. The three nitrogen atoms of the anionic azide were easily located. The absence of additional peaks of any consequence tended to support the choice of $Pnam$ as the most probable space group. A new set of parameters was obtained from the first Fourier synthesis and used to calculate a second Fourier synthesis based on the phases calculated by using all eleven independent atoms.

The position parameters from the second Fourier synthesis, parameter set I, were used as the starting parameters for a series of least-squares calculations. The quantity minimized in the least-squares calculation was $\Sigma w(F_o - F_c)^2$, the weighting function being given below. A total of five cycles was computed, using the full matrix and only the observed reflections. The final set of parameters was called parameter set II.

A difference Fourier synthesis was calculated using parameter set II and all the observed reflections to see if any information concerning the hydrogen atoms could be obtained. The difference Fourier synthesis gave a number of peaks of moderate height, but these were of more or less a random nature. A large positive peak at the position of the cobalt atom was quite evident, and the effect of varying the f curve for cobalt was next investigated.

The f curve for cobalt used in the calculations was for Co^{3+} from Thomas & Umeda (1957). There was some question as to the validity of this choice, there-

Table 1. *The final heavy-atom parameters and their standard deviations (in parenthesis)*

All values for the nitrogen atoms have been multiplied by 10^{+4}. The temperature factor is of the form
$$T_i = \exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\right]$$

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	2657 (3)	3661 (5)	2500*	30 (2)	92 (6)	102 (5)	−4 (6)	0*	0*
N(2)	2704 (5)	5163 (5)	2500*	41 (3)	93 (6)	94 (5)	−5 (6)	0*	0*
N(3)	2802 (5)	6579 (7)	2500*	79 (5)	108 (7)	209 (10)	−32 (10)	0*	0*
N(4)	0508 (4)	4486 (5)	2500*	42 (3)	93 (6)	77 (4)	19 (6)	0*	0*
N(5)	0103 (4)	1070 (5)	2500*	41 (3)	99 (6)	72 (4)	−17 (6)	0*	0*
N(6)	2210 (4)	0435 (5)	2500*	51 (3)	83 (6)	80 (4)	28 (5)	0*	0*
N(7)	1401 (2)	2449 (3)	0618 (3)	36 (1)	118 (3)	63 (2)	9 (5)	4 (3)	4 (6)
N(8)	3826 (3)	0970 (4)	0387 (4)	68 (3)	124 (5)	102 (4)	−9()6)	31 (5)	−15 (7)
N(9)	3975 (2)	2260 (4)	−0074 (3)	41 (1)	134 (5)	69 (2)	−4 (5)	−17 (3)	0 (6)
N(10)	4148 (4)	3580 (5)	−500 (5)	84 (3)	198 (8)	144 (6)	−63 (8)	−53 (7)	155 (11)
Co†	13627 (4)	24503 (8)	2500*	271 (3)	699 (8)	502 (5)	18 (10)	0*	0*

* These parameters are determined by symmetry.   † Values for cobalt are times 10^{+5}.

Table 2. *List of observed and calculated structure factors*

The scale is 100 times the absolute scale. A negative *F* (observed) indicates a 'less than'

Table 2 (cont.)

fore the Co^0 curve of Freeman & Watson (1961) was used in the subsequent calculations. The nitrogen curve of Hoerni & Ibers (1954) was retained.

Three cycles of least squares were computed with the use of parameter set I as the initial values. The final set of parameters, parameter set III, was used to calculate a second difference Fourier synthesis. The second difference Fourier synthesis was almost identical with the first.

A survey of the 1412 observed reflections revealed that many of the weak reflections were in poor agreement, even though the overall R was about 8%. The Fourier routine was modified to reject all reflections if $4\Delta F$ was greater than F(observed). This modification led to a definite improvement in the difference map, although some objectionable features remained. Tentative positions for the hydrogen atoms were chosen by assuming an N–H distance of 1·0 Å and tetrahedral symmetry around the nitrogen atoms and by attempting to find the best fit with peaks in the difference Fourier synthesis.

With parameter set III as the starting values, three additional cycles of least squares were computed. The hydrogen atoms were included in the structure factor calculation, but only the heavy atom parameters were refined. The final result was parameter set IV.

A final set of least-squares calculations was carried out with a change in the weighting system and using only selected reflections. In all previous computations, the following weighting scheme had been employed:

$$\text{if} \quad F_o \leq F_{min} \qquad \sqrt{w} = 1\cdot0$$
$$\text{if} \quad F_o > F_{min} \qquad \sqrt{w} = F_{min}/F_o$$

where F_{min} was chosen as 24·7. The weighting was changed to:

$$\text{if} \quad F_o < F_{low} \qquad \sqrt{w} = F_o/F_{low}$$
$$\text{if} \quad F_{up} > F_o > F_{low} \qquad \sqrt{w} = 1\cdot0$$
$$\text{if} \quad F_o > F_{up} \qquad \sqrt{w} = F_{up}/F_o$$

where F_{up} was 24·7 and F_{low} was 4·9. In addition only the observed reflections where $5\Delta F < F_o$ were included in the computation. A total of five least-squares cycles was computed before the shifts were less than the standard deviations obtained from the inverse matrix. The final parameters, set V, are given in Table 1. The errors quoted in Table 1 were obtained by standard procedures from the inverse of the full matrix formed in obtaining parameter set V.

The set of structure factors calculated with parameter set V is given in Table 2. The negative F(obs.) indicates the reflections which were observed to be 10% or less above the background level. These reflections were then given the value of 5% of the background for the particular 2θ value.

The thermal parameters for the cobalt atom and the ten nitrogen atoms were used to calculate the mean square displacements for each atom. The values of

Table 3. *Principal-axis parameters of the atomic vibration ellipsoids*

Atom	i	$\sqrt{(\overline{r_i^2})}$	q_{ia}	q_{ib}	q_{ic}
Co	1	0·166	0·0000	0·0000	1·0000
	2	0·153	−0·8206	−0·5715	0·0000
	3	0·150	−0·5715	0·8206	0·0000
N(1)	1	0·237	0·0000	0·0000	1·0000
	2	0·174	0·1945	−0·9809	0·0000
	3	0·159	0·9809	0·1945	0·0000
N(2)	1	0·228	0·0000	0·0000	1·0000
	2	0·188	0·9588	−0·2840	0·0000
	3	0·173	0·2840	0·9588	0·0000
N(3)	1	0·339	0·0000	0·0000	1·0000
	2	0·264	0·9718	−0·2360	0·0000
	3	0·182	0·2360	0·9718	0·0000
N(4)	1	0·205	0·0000	0·0000	1·0000
	2	0·196	−0·8542	−0·5199	0·0000
	3	0·166	−0·5199	0·8542	0·0000
N(5)	1	0·199	0·0000	0·0000	1·0000
	2	0·196	0·7971	−0·6038	0·0000
	3	0·170	0·6038	0·7971	0·0000
N(6)	1	0·210	0·0000	0·0000	1·0000
	2	0·212	−0·9658	−0·2594	0·0000
	3	0·161	−0·2594	0·9658	0·0000
N(7)	1	0·199	−0·3016	−0·9241	−0·2347
	2	0·186	−0·1956	0·3009	−0·9334
	3	0·173	−0·9332	0·2356	0·2715
N(8)	1	0·262	−0·7356	0·1346	−0·6638
	2	0·216	−0·6768	−0·1052	0·7286
	3	0·200	−0·0282	−0·9853	−0·1686
N(9)	1	0·210	−0·2942	0·9079	0·2988
	2	0·206	−0·5371	−0·4156	0·7340
	3	0·175	−0·7906	−0·0555	−0·6099
N(10)	1	0·344	0·4646	−0·5621	−0·6842
	2	0·243	0·8828	0·2342	0·4071
	3	0·195	0·0686	0·7932	−0·6051

the mean square displacements and their direction cosines are given in Table 3.

Results

Intramolecular distances and angles

The azidopentamminecobalt(III) cation is illustrated in Fig. 1. The pertinent intramolecular distances for
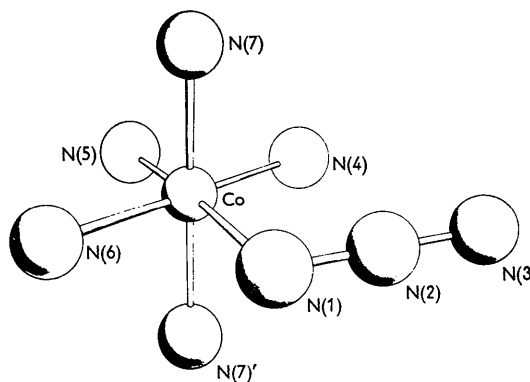

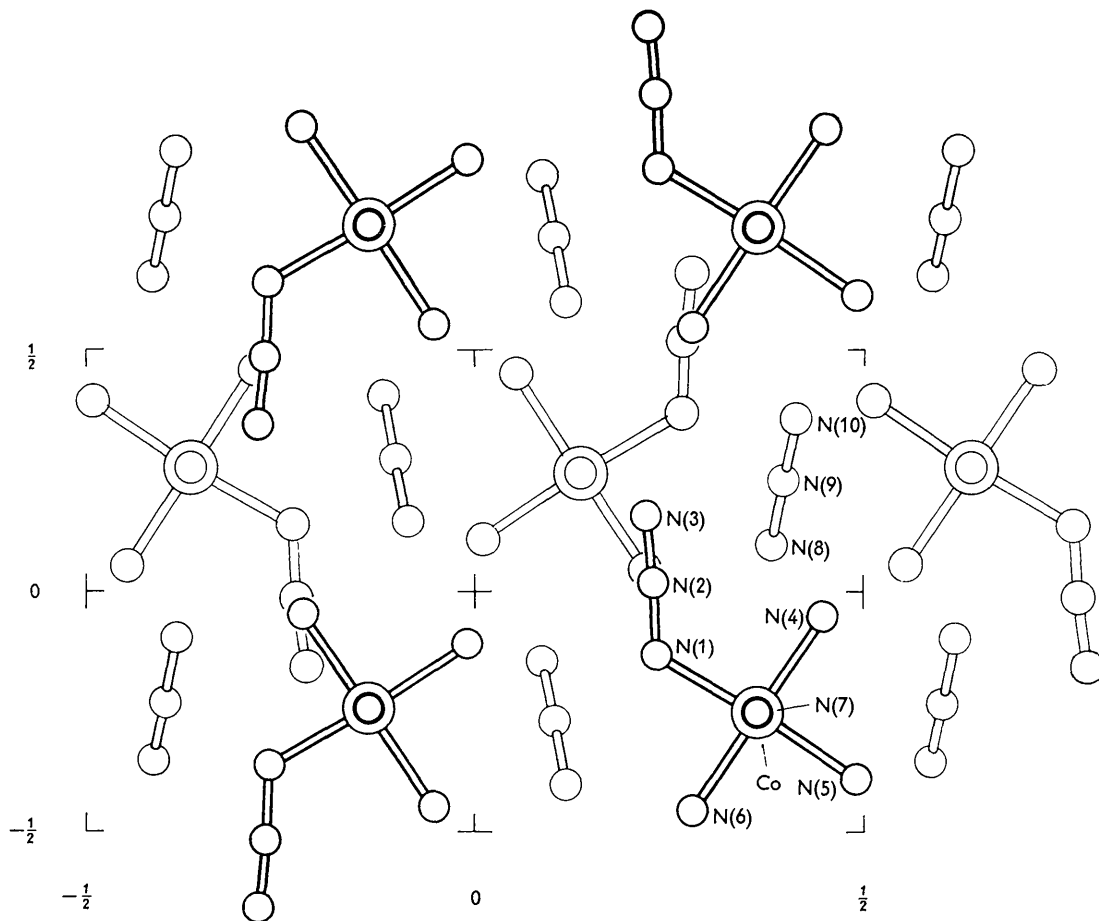Fig. 1. Perspective view of the azidopentamminecobalt(III) cation.

Fig. 2. Projection of the structure on (001). The numbering of the cobalt atom and nitrogens 1-7 corresponds to the position $\frac{1}{2}-x$, $\frac{1}{2}+y-1$, $\frac{1}{2}+z$ relative to the parameters in Table 1.

Table 4. *Intramolecular distances and angles*

Atoms	Distance*	Atoms	Angle†
Co–N(1)	1·943 Å	Co–N(1)–N(2)	125·2°
Co–N(4)	1·976	Co–N(1)–N(3)	124·8
Co–N(5)	1·977	N(1)–Co–N(4)	94·2
Co–N(6)	1·957	N(4)–Co–N(5)	89·9
Co–N(7)	1·960	N(5)–Co–N(6)	90·1
N(1)–N(2)	1·208	N(6)–Co–N(1)	85·8
N(2)–N(3)	1·145	N(1)–Co–N(7)	88·8
N(1)–N(4)	2·870	N(4)–Co–N(7)	90·9
N(4)–N(5)	2·794	N(5)–Co–N(7)	91·2
N(5)–N(6)	2·786	N(6)–Co–N(7)	89·1
N(6)–N(1)	2·655	N(1)–N(2)–N(3)	179·3
N(1)–N(7)	2·730	N(8)–N(9)–N(10)	177·5
N(4)–N(7)	2·804		
N(5)–N(7)	2·813		
N(6)–N(7)	2·749		
N(4)–N(2)	2·905		
N(4)–N(3)	3·429		
N(8)–N(9)	1·158		
N(9)–N(10)	1·172		

* The standard deviation is 0·005 Å for the Co–N bonds and 0·007 Å for the N–N bonds.

† The standard deviation for the angles involving the Cobalt is 0·2° and for the two azide angles 0·3°.

the cation and anion were calculated using parameter set V and are given in Table 4. The average of the four independent cobalt–ammine bonds is $1·968 \pm 0·006$ Å. This average value compares favorably with the value of 1·97 Å obtained by averaging the various cobalt(III)–ammine distances reported by Sutton (1958) and the value of 1·96 Å reported by Viswanathan & Kuncher (1961) for the distances in cobalt(III) bis(dimethylgloximino)diammine nitrate. The fact that the cobalt(III)–azide bond distance of 1·943 Å is significantly shorter than the cobalt(III)–ammine bonds is not surprising. The hybridization of the nitrogen atom in the two cases is different and quite likely accounts for the difference in bond distances. A similar effect is observed in the case of carbon–carbon single bonds.

The azide anion is slightly bent with nitrogen–nitrogen distances of 1·158 and 1·172 Å, the average being 1·165 Å. The two nitrogen–nitrogen distances can be considered equal within the experimental error. The values observed in earlier crystal structure determinations of ionic azides are summarized by

Evans, Yoffe & Gray (1959) and give an average value of $1 \cdot 154 \pm 0 \cdot 015$ Å in excellent agreement with the above experimental value. The azide in the coordination sphere is definitely asymmetric, with nitrogen–nitrogen distances of $1 \cdot 208$ and $1 \cdot 145$ Å. This azide is more symmetrical than the azide group found in cyanuric triazide by Knaggs (1935) ($1 \cdot 26$ and $1 \cdot 11$ Å), in methyl azide by Livingston & Rao (1960) ($1 \cdot 24$ and $1 \cdot 12$ Å), and in hydrazoic acid by Amble & Dailey (1950) ($1 \cdot 240$ and $1 \cdot 134$ Å). The bond angle $124 \cdot 8°$ of Co–N(1)–N(3) in the coordinated azide is larger than the angle found in any of the covalent azides reported in the literature.

Intermolecular distances and packing

A view of the structure down the c axis is given in Fig. 2. The numbering of the Co atom and nitrogen atoms 1–7 in Fig. 2 corresponds to the position $\frac{1}{2}-x$, $\frac{1}{2}+y-1$, and $\frac{1}{2}+z$ relative to the parameters in Table 1. The intermolecular distances are given in Table 5.

Table 5. *Intermolecular distances**

From atom X in molecule A	To atom Y in molecule		Distance
N(4)	N(8)	C	$3 \cdot 348 \pm 0 \cdot 007$ Å
N(4)	N(9)	C	3·435
N(4)	N(10)	C	3·918
N(4)	N(8)	B	3·124
N(4)	N(9)	B	3·622
N(5)	N(1)	B	3·187
N(5)	N(2)	B	3·271
N(5)	N(3)	B	3·664
N(5)	N(8)	B	3·640
N(5)	N(9)	B	3·336
N(5)	N(10)	B	3·374
N(5)	N(10)	D	3·046
N(6)	N(8)	A	3·071
N(6)	N(9)	A	3·820
N(6)	N(9)	D	3·907
N(6)	N(10)	D	3·110
N(7)	N(8)	A	3·376
N(7)	N(9)	A	3·426
N(7)	N(10)	A	3·864
N(7)	N(8)	B	3·588
N(7)	N(9)	B	3·242
N(7)	N(10)	B	3·258

* Molecule A is at x, y, z (Table 1), B at ($\frac{1}{2}+x-1$, $\frac{1}{2}-y$, z), C at ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\bar{z}$) and D at ($\frac{1}{2}-x$, $\frac{1}{2}+y-1$, $\bar{z}$).

The cations are located in the mirror planes at $z=\frac{1}{4}$ and $z=\frac{3}{4}$. The xy coordinates of the cobalt atom are approximately $\frac{1}{8}, \frac{1}{4}$; thus any one cation is almost equidistant from the eight neighbors located in the mirror planes above and below the cation. The above arrangement of cations produces holes of approximately tetrahedral character. Each of these holes is filled with an azide centered at approximately $z=0$ and $z=\frac{1}{2}$. The resulting structure is reasonably close-packed considering the non-spherical nature of the anions and cations.

The cations in the mirror planes are apparently linked through a hydrogen bond between N(1) and N(5). The difference Fourier syntheses give some evidence that there is a hydrogen bonded to N(5) and oriented toward N(1). The two remaining hydrogen atoms on N(5) appear to be directed toward N(10) of the anionic azide located on either side of the mirror plane. If one considers N(4), N(6), and N(7), there are also possible hydrogen bonds to the neighboring azide anions. Because definite positions for the hydrogens could not be obtained from the difference Fourier syntheses, the location of the hydrogen bonds cannot be assigned with certainty.

Discussion

Reliability of the data

The stationary-crystal technique for measuring intensities with a proportional counter has not been widely used to date. The present results appear to indicate that the intensity data obtained in this manner can be sufficiently precise. The main concerns with this technique are to insure that an area of uniform sensitivity of the counter is located behind the counter window and that the intensity output of the source is reasonably uniform. The advantage of the stationary crystal technique is the ease and speed with which one can measure the intensities of a large number of diffraction maxima.

Since the weaker reflections were measured by the time required to accumulate 400 counts, these data will probably be less precise. Therefore the weighting scheme finally employed was considered to be the most reasonable. The reflections must not be weighted according to the usual criteria of counting statistics where $\sigma = \sqrt{N}$ counts, since the reflections of highest intensity are most affected by extinction. The alternative of measuring all reflections for the same number of counts (*i.e.* 1000) and using a unit weight is not too practical. If a large number of reflections from a moderately complex crystal are to be measured, the majority of the maxima will be of low intensity and will require long counting times.

Two features of the data deserve further comment: the relatively high value of the residual R and the insensitivity of the parameters to the model chosen. The high value of R is due in part to the large number of low intensity reflections which cannot be determined accurately. Because of the nature of the experimental set-up, the shape of the crystal will also affect the accuracy of the intensity measurements. The fact that changing the scattering curve from neutral cobalt to cobalt plus three has little effect on the parameters is not surprising. A comparison of the scattering factors for Co^0 and Co^{3+} reveals that they are quite similar after $\sin \theta / \lambda$ equals 0·25, and, in fact, the majority of the intensity data has a value of $\sin \theta / \lambda$ greater than 0·25. The fact that a change in the weights produces little effect supports the feeling that the errors in the data are random.

Nature of the coordinated azide group

The presence of both anionic and coordinated azides in the crystal lattice permits a comparison of the bonding in the two forms. The present study has demonstrated that an azide group coordinated to a cobalt ion is distorted compared with an isolated symmetric azide anion. The distortion of the azide group is not as severe as if the azide were bonded to a carbon or hydrogen atom. In the case of coordination to a cobalt atom, the bond angle R–N–N is also increased. Crystal packing does not usually produce significant changes in the bond distances, therefore the asymmetry of the azide group is a direct consequence of the nature of the cobalt–azide bond.

A simple explanation for the above observations regarding distances and angles in the coordinated azide group is that resonance occurs between a state $Co-N_3$ and a second state $Co^+N_3^-$. Resonance between the two states results in a more symmetric azide with a larger bond angle R–N–N than in the case where the non-ionic form predominates in the ground state.

This study represents the first structure determination of a coordinated azide; thus there are no similar structures to which it can be compared. We are attempting to prepare the corresponding chromium salt for comparison with the cobalt salt. In addition samples of *m*- and *p*-azidonitrobenzene are available and will be studied in the future to investigate possible resonance of the azide group with the benzene ring.

References

AMBLE, E. & DAILEY, B. P. (1950). *J. Chem. Phys.* **18**, 1422.

EVANS, B. L., YOFFE, A. D. & GRAY, P. (1959). *Chem. Revs.* **59**, 515.

FREEMAN, A. J. & WATSON, R. E. (1961). *Acta Cryst.* **14**, 231.

FUJITA, J., NAKAMOTO, K. & KOBAYSHI, M. (1956). *J. Amer. Chem. Soc.* **78**, 3295.

HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.

KNAGGS, I. E. (1935). *Proc. Roy. Soc.* A, **150**, 576.

LINHARD, M. & BARTHOLD, W. (1958). *Z. anorg. Chem.* **279**, 173.

LINHARD, M., SIEBERT, H. & WEIGEL, M. (1958). *Z. anorg. Chem.* **278**, 287.

LIVINGSTON, R. L. & RAO, C. N. R. (1960). *J. Phys. Chem.* **64**, 756.

STAPLES, P. J. & TOBE, M. L. (1960). *J. Chem. Soc.* p.4812.

SUTTON, L. E. (editor), (1958). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* London: The Chemical Society.

THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

VISWANATHAN, K. S. & KUNCHUR, N. R. (1961). *Acta Cryst.* **14**, 675.

The Crystal and Molecular Structure of *cis*-1,2-Acenaphthenediol Dinitrate

By THOMAS C. W. MAK AND JAMES TROTTER

Department of Chemistry, The University of British Columbia, Vancouver, Canada

The crystal and molecular structure of *cis*-1,2-acenaphthenediol dinitrate has been determined by Patterson methods, and refined by $(F_o - F_c)$ syntheses using partial three-dimensional data. The crystals are monoclinic with four molecules in a unit cell of dimensions

$$a = 17\cdot10 \pm 0\cdot02, \quad b = 4\cdot242 \pm 0\cdot005, \quad c = 19\cdot18 \pm 0\cdot02 \text{ Å}; \quad \beta = 122° \, 12' \pm 5',$$

the space group being $P2_1/c$.

The carbon skeleton is planar, with dimensions very similar to those found in other compounds containing the acenaphthene system. The C(1)–C(2) bond in the *peri*-ring has a length of 1·60 Å which is significantly longer than a normal aliphatic single bond. There is no bonding between the nitroxy groups, which are planar and inclined at angles of +62·1° and +71·2° to the plane of carbon atoms. The average bond distances are: C–O, 1·47; O–N, 1·41; N=O, 1·19 Å. All intermolecular contacts are normal.
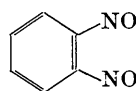
Introduction

Recently it has been demonstrated that *o*–dinitrosobenzene (I) has the benzofurazan-*N*-oxide (II) structure in the solid state (Hulme, 1962). A tautomeric form (III) in which the nitroxy groups are directly
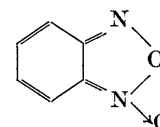

(I)   (II)