Accuracy of a Crystal Structure Determination

The Structure of Carbonato-Tetrammine-Cobalt (III) Bromide

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Two-dimensional refinements have been carried out on the structure of [Co(NH$_3$)$_4$CO$_3$]Br with data obtained by different groups of workers. Comparison of the different coordinates obtained indicates that in structure determinations using photographic techniques and two-dimensional methods, heavy atoms may be located with r.m.s. errors of 0.01 Å while light atoms may be subject to coordinate r.m.s. errors of 0.05—0.08 Å. Considerations of bond length variations of less than 0.1 Å must be based upon three-dimensional data to carry significance.

Barclay and Hoskins[1] determined recently the crystal structure of [Co(NH$_3$)$_4$CO$_3$]Br. Some time before their paper appeared we started upon an X-ray investigation of this compound too. We have found it worthwhile to make a comparison between the two sets of independent data and to refine our data in a different way in order to test accuracy and reliability of commonly used methods.

Barclay and Hoskins obtained three-dimensional data using Weissenberg techniques and visually measured intensities. They employed Co$K\alpha$ radiation and measured 459 reflexions. We measured intensities from two zones only:

92 0kl reflexions were measured photometrically from integrated Weissenberg films (Co-radiation) and 74 hk0 reflexions were measured visually from Precession photographs (Mo-radiation). The usual corrections were made by computation on a digital computer. Both sets of data were uncorrected for absorption and extinction.

Barclay and Hoskins recorded 96 0kl reflexions. Six of these are not visible on our photographs and we measured intensities of two reflexions not observed by them. They measured 56 hk0 reflexions. Seven of these were not visible on our Precession patterns.

For easy comparison we denote the data of Barclay and Hoskins with index I and our own data with index II. The agreement between structure

amplitudes measured by both groups of workers may be expressed by the indexes:

$$r = \Sigma|F_{\mathrm{I}} - kF_{\mathrm{II}}|/\Sigma|F_{\mathrm{I}}|; \quad r_{0kl} = 11.1 \% \quad r_{hk0} = 8.9 \%$$

A closer study of individual discrepancies between the two sets of experimental data and of calculated structure factors indicated that four of our $0kl$ reflexions and one $hk0$ reflexion were affected by extinction. The data of Barclay and Hoskins were less affected by this error.

New agreement indexes were calculated for observations not including intensities affected by extinction.

For 86 $0kl$ reflexions we obtained $r_{0kl} = 10.0 \%$

For 48 $hk0$ reflexions: $r_{hk0} = 8.6 \%$

Barclay and Hoskins employed two crystals for their investigation of cross sections 0.06×0.08 mm^2 and 0.07×0.08 mm^2. We used one crystal with cross section 0.07×0.05 mm^2.

The linear absorption coefficient is 126.7 cm^{-1} for Co$K\alpha$ radiation and 69.9 for Mo$K\alpha$ radiation.

Apparently corrections for extinction are more important than are corrections for absorption.

The following lattice constants were reported in Ref.[1]

$a = 7.629 \pm 0.005$ Å $\qquad b = 16.886 \pm 0.010$ Å $\qquad c = 6.760 \pm 0.005$ Å

The space group is *Pmnb*.

Our crystal setting differs from that of Barclay and Hoskins who use the space group symbol *Pcmn*.

REFINEMENT

Barclay and Hoskins refined the structure from successive three-dimensional Fourier synthesis. They used an over all isotropic temperature factor in the structure factor calculations and stopped at an R-factor of 12 %. This refinement is called 1 for reference. The results are given in Table 1.

For refinement we used a method suggested by Bhuiya and Stanley [2] which appears promising for projections with overlapping atoms. The geo-

Table 1. Data of Barclay and Hoskins.

	x/a	y/b	z/c	B Å^2	σ r.m.s. Å
Br	0.2500	0.2758	0.5426	3.00	0.002
Co	0.2500	0.0903	0.1173	3.00	0.003
N(1)	0.2500	0.2003	0.0273	3.00	0.014
N(2)	0.2500	0.4805	0.3032	3.00	0.017
N(3)	0.0548	0.1118	0.3145	3.00	0.021
C	0.2500	0.0446	−0.2053	3.00	0.015
O(1)	0.2500	0.0166	−0.3745	3.00	0.013
O(2)	0.1061	0.0637	−0.1032	3.00	0.010

$R = 12 \%$

metric and the thermal parameters of each atom of the structure are varied in turn and the parameters yielding the lowest R-value are chosen. For the computations we used an Algol programme written for the computer GIER. The programme refines two geometric parameters and one individual isotropic B-factor for each atom of the structure.

For the structure factor calculations we employed the approximation:

$$f_n(\sin\Theta/\lambda) = A_n\exp[-a_n(\sin\Theta/\lambda)^2] + B_n\exp[-b_n(\sin\Theta/\lambda)^2] + C_n\exp[-c_n(\sin\Theta/\lambda)^2]$$

using the parameters listed by Forsyth and Wells [3].

The scattering curves of cobalt and bromine were corrected for dispersion for cobalt radiation using $\Delta f_{Co} = -2.61$, $\Delta f_{Br} = -1.46$.

The following sets of data have been refined by the Bhuiya-Stanley method:
2) Data of Barclay and Hoskins:
   96 $0kl$ reflexions; 56 $hk0$ reflexions.
   Results are given in Table 2.
3) Own experimental data:
   a) 90 observed $0kl$ reflexions and 6 non observed reflexions given half the value of the smallest observed structure factor. 49 observed $hk0$ reflexions and seven none observed treated as above. Results are given in Table 3a.
   b) 88 observed $0kl$ reflexions; 4 reflexions suspected of extinction and none observed reflexions left out.
   73 $hk0$ reflexions; one suspected for extinction and none observed reflexions left out.
   Results are given in Table 3b.

In all the refinements the coordinates reported by Barclay and Hoskins were used as starting points. The usual R-indexes:

$$\Sigma||F_o| - |kF_c||/\Sigma|F_o| \text{ are given in Table 4.}$$

The standard deviations given for the two-dimensional refinements were calculated from formulae valid for least squares methods employing weights of unity.

Table 2. Data of Barclay and Hoskins.

	$hk0$(Co) 56 reflexions							$0kl$(Co) 96 reflexions					
	x/a	σx	y/b	σy	B	σB	y/b	σy	z/c	σz	B	σb
		Å		Å	Å²	Å²		Å		Å	Å²	Å²
Br	0.2500		0.2764	0.013	1.75	0.3	0.2760	0.007	0.5440	0.007	2.70	0.2
Co	0.2500		0.0914	0.018	1.10	0.4	0.0905	0.010	0.1195	0.009	1.45	0.2
N(1)	0.2500		0.1997	0.086	2.20	2.3	0.2029	0.041	0.0222	0.040	1.75	1.0
N(2)	0.2500		0.4807	0.085	1.95	2.2	0.4835	0.046	0.3055	0.047	2.90	1.3
N(3)	0.0549	0.060	0.1143	0.061	2.10	1.5	0.1133	0.026	0.3096	0.025	3.60	0.7
C	0.2500		0.0469	0.135	4.45	4.0	0.0425	0.046	−0.2057	0.047	1.40	1.1
O(1)	0.2500		0.0127	0.096	4.80	2.8	0.0159	0.039	−0.3713	0.040	3.25	1.1
O(2)	0.0952	0.048	0.0650	0.049	2.00	1.2	0.0635	0.019	−0.1085	0.018	2.80	0.5

$$R = 11.79 \% \qquad\qquad R = 8.39 \%$$

Table 3a. Data of Haagensen and Rasmussen.

	hk0(Mo) 56 reflexions						0kl(Co) 96 reflexions					
	x/a	σx	y/b	σy	B	σB	y/b	σy	z/c	σz	B	σB
		Å		Å	Å²	Å²		Å		Å	Å²	Å²
Br	0.2500		0.2765	0.013	1.95	0.3	0.2761	0.009	0.5456	0.009	1.50	0.2
Co	0.2500		0.0908	0.014	0.70	0.3	0.0907	0.011	0.1205	0.011	−0.05	0.2
N(1)	0.2500		0.2023	0.121	4.75	3.7	0.2064	0.045	0.0275	0.044	−0.30	1.1
N(2)	0.2500		0.4809	0.099	2.55	2.6	0.4874	0.073	0.3107	0.075	3.40	2.0
N(3)	0.0626	0.062	0.1102	0.067	1.80	1.4	0.1160	0.034	0.3098	0.032	2.35	0.9
C	0.2500		0.0492	0.118	2.65	3.2	0.0408	0.048	−0.2070	0.049	−0.85	1.1
O(1)	0.2500		0.0135	0.086	3.10	2.3	0.0142	0.054	−0.3802	0.056	2.70	1.4
O(2)	0.0985	0.049	0.0651	0.050	1.60	1.2	0.0643	0.023	−0.1069	0.022	1.00	0.5

$R = 10.14\ \%$ $R = 11.19\ \%$

Table 3b. Data of Haagensen and Rasmussen.

	hk0(Mo) 73 reflexions						0kl(Co) 88 reflexions					
	x/a	σx	y/b	σy	B	σB	y/b	σy	z/c	σz	B	σB
		Å		Å	Å²	Å²		Å		Å	Å²	Å²
Br	0.2500		0.2762	0.007	2.35	0.2	0.2763	0.006	0.5458	0.006	2.00	0.1
Co	0.2500		0.0908	0.008	1.15	0.1	0.0905	0.007	0.1187	0.007	0.60	0.2
N(1)	0.2500		0.2011	0.081	5.90	2.5	0.2036	0.032	0.0164	0.033	1.10	0.8
N(2)	0.2500		0.4817	0.050	1.90	1.1	0.4862	0.036	0.3056	0.035	1.65	0.9
N(3)	0.0656	0.041	0.1104	0.041	3.05	0.9	0.1155	0.020	0.3053	0.021	2.60	0.5
C	0.2500		0.0543	0.055	1.80	1.3	0.0449	0.030	−0.2046	0.030	−0.55	0.7
O(1)	0.2500		0.0133	0.045	2.30	1.0	0.0181	0.037	−0.3582	0.037	3.65	1.0
O(2)	0.1109	0.032	0.0639	0.030	2.40	0.7	0.0646	0.014	−0.1081	0.013	1.20	0.3

$R = 8.14\ \%$ $R = 7.33\ \%$

CONCLUSIONS

From the standard deviations one must conclude that the parameters from the three-dimensional data (1) of Barclay and Hoskins are the most accurate set available. Because many atoms have a special parameter in the xy projection we shall discuss the two projections separately.

Using the same number of reflexions (56) the data obtained with Co-radiation give on the average almost the same standard deviations as the data obtained with Mo-radiation. Increasing the number of reflexions from 56 to 73 cause the average standard deviations of the light atoms excluding Co and Br to decrease from 0.09 Å to 0.05 Å.

For the yz projections we have compared the differences between the various sets of geometric parameters with the standard deviations. We denote standard deviations with σy and σz as usual and numerical differences between different sets of parameters with Δy and Δz.

Table 4.

	Before refinement		After refinement	
	$R(0kl)$;	$R(hk0)$	$R(0kl)$;	$R(hk0)$
2	12.40 %	18.34 %	8.39 %	11.79 %
3a	20.70 %	16.78 %	11.19 %	10.14 %
3b	15.35 %	16.01 %	7.33 %	8.14 %

Table 5.

	$\sigma y \approx \sigma z$		$\Delta y \approx \Delta z$
	Å		Å
1	0.006	1 − 2	0.026
2	0.037	1 − 3a	0.047
3a	0.046	1 − 3b	0.047
3b	0.028	2 − 3b	0.030

The heavy atoms Co and Br can be located rather precisely with any of the sets of data. The deviations between the different sets of parameters are of the order of magnitude 0.01 Å.

The averages found for the light atoms excluding Co and Br are given in Table 5.

From the values of the standard deviations we may conclude that photo-metrically measured intensities result in slightly better atomic coordinates than do visually determined intensities but only if data affected by extinc-tion are left out of computations. Two-dimensional data will have to attain a very high degree of accuracy to be able to compete with visually determined three-dimensional data.

The differences 1−2, are probably smaller than 1−3b, because the data of 2 are partly the same as the data of 1. The differences 2−3b, are approxi-mately equal to the standard deviations of 3b. It appears to be a good approxi-mation to use the values of $|F_o - F_c|$ as a measure of experimental accuracy of F_o in well refined structures in the computations of standard deviations.

The individual differences 1−2 *etc.* are in most cases within the standard deviations. A few exceptions occur: The y coordinate of the N(2)-atom tends to be increased significantly in all $0kl$ refinements but not in the $hk0$ refinements. No other systematic variations occur although a few individual discrepancies are notable such as the variation of the y-parameter of the carbon atom.

Our results indicate that in structure determination with atoms of varying atomic weights and using photographic methods, heavy atoms may be located quite accurately (r.m.s. 0.01 Å) by two-dimensional methods while lighter atoms may be subject to r.m.s. errors of about 0.05−0.08 Å. For light atoms discussions of bond length variations of less than 0.1 Å will probably have to be based upon three-dimensional data to carry significance.

The variation of temperature factors shows that no physical significance should be attached to these values.

Our conclusions are in agreement with results of other two-dimensional refinements which at present are carried out in this laboratory.

REFERENCES

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