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The Crystal Structure of Sodium Bromide Dihydrate

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$NaBr.2H_2O$ is monoclinic, $P2_1/c$, $Z=4$, with $a=6{\cdot}575$, $b=10{\cdot}456$, $c=6{\cdot}776$ Å and $\beta=113{\cdot}38°$. The structure agrees very well with that determined independently by Culot, Piret & Van Meersche (1962); the differences are attributed chiefly to different absorption errors.

Introduction

The crystal structure of sodium bromide dihydrate has been investigated in order to study the role of hydrogen bonding in alkali halide hydrates and to make possible a more detailed analysis of the infrared absorption of the solid (Schiffer & Hornig, 1961). During the final stages of refinement, we learned that Culot, Piret & Van Meersche (1962) had just completed determination of the same structure. Comparison of the two independent studies shows several interesting features.

Structure determination

Details of the present work are described in a thesis (Haaf, 1963). $NaBr.2H_2O$ is monoclinic, space group $P2_1/c$, with 4 formula units per cell. The cell dimensions are $a=6{\cdot}575$ (0·002), $b=10{\cdot}456$ (0·005), $c=6{\cdot}776$ (0·002) Å and $\beta=113{\cdot}38$ (0·02)°. The values in parentheses are standard deviations measuring internal consistency only; the systematic error may be two or three times as large. These results agree well

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with those of Culot, Piret & Van Meersche (1962), hereafter referred to as CPV.

The single crystal used for all intensity measurements was a cylinder 0·19 mm in diameter, grown and preserved in a thin-walled Pyrex glass capillary. Intensities were collected by Weissenberg and precession recording, using chiefly Mo $K\alpha$ radiation. Visual estimation was used for the former, microphotometer measurement for the latter.

The structure was determined from a three-dimensional Patterson synthesis which readily located the bromine atom. Subsequent electron density and difference maps located the other atoms and refined the structure. The final refinement was by means of least squares, the computer program of Carpenter (1963) being used.

The final results are included in Tables 1, 2 and 3. In each, quantities in parentheses are internal estimates of standard deviations, calculated from diagonal elements of the matrix of the least-squares normal equations; accordingly they are somewhat too small.

Table 1. *Atomic coordinates for* $NaBr.2H_2O$

Atom	Coordinate	CPV	Present work
Br	x	0·2965	0·2964 (0·0002)
	y	0·1191	0·1191 (0·0001)
	z	0·2120	0·2120 (0·0002)
Na	x	0·0155	0·0146 (0·0007)
	y	0·1679	0·1693 (0·0005)
	z	0·4576	0·4566 (0·0007)
O(1)	x	0·7907	0·7882 (0·0012)
	y	0·3132	0·3132 (0·0009)
	z	0·1761	0·1762 (0·0013)
O(2)	x	0·1262	0·2130 (0·0011)
	y	0·4922	0·4900 (0·0008)
	z	0·2195	0·2199 (0·0013)

Table 2. *Temperature factor parameters for* $NaBr.2H_2O$

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{31}$
Br	240 (2)	84 (1)	186 (2)	188 (3)
Na	252 (12)	77 (5)	180 (11)	126 (18)
O(1)	205 (18)	83 (10)	221 (21)	91 (30)
O(2)	206 (18)	83 (10)	229 (20)	161 (28)

Table 3. *Interatomic distances in* $NaBr.2H_2O$

	CPV	This work
Distances from a sodium ion		
to oxygen	2·37	2·40 (0·009)
	2·40	2·41 (0·009)
	2·48	2·50 (0·011)
	2·42	2·42 (0·009)
to bromine	2·96	2·96 (0·005)
	2·98	2·98 (0·006)
Shortest O · · · Br distances		
	3·32	3·36 (0·008)
	3·37	3·36 (0·009)
	3·36	3·38 (0·010)

Comparison between independent determinations

Final atomic coordinates obtained in the present work are compared with those of CPV in Table 1. Although the estimated standard deviations (σ) of the present study are somewhat optimistic, half of the coordinates from the two studies differ by less than σ and none differ by as much as 3σ. The agreement in coordinates is thus quite good despite differences in refinement; in particular, anisotropic temperature factors were used in the present refinement, isotropic in that of CPV.

In order to compare the two results in more detail, the data of CPV were subjected to further refinement with use of anisotropic temperature factors. The conventional discrepancy factor, including unobserved reflections, decreased from 12·4 (recalculated) to 11·0%. The shifts in the coordinates, however, were rather small and did not improve the agreement with the results of the present work.

Final discrepancy factors, for observed reflections only, for the two determinations are 10·0% for CPV and 6·2% for the present work, both after anisotropic refinement. These are not quite comparable because the CPV data includes more very faint reflections. We believe, however, that the major source of this difference is different absorption error. No absorption correction was made in either case, and the consequences are more severe for the parallelepipedal crystal and copper radiation of CPV than for the cylindrical crystal and molybdenum radiation of the present work. This suggestion is supported by the fact that the temperature factor parameters from the anistropic refinement of the CPV data are typically somewhat smaller than in the present work. For this reason, detailed comparison of temperature parameters from the two studies would have little meaning. For the present work, the parameters in the expression

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{31}lh)\right]$$

are reported in Table 2.

Comparisons of the most important interatomic distances are shown in Table 3. The differences are rather slight and suggest no changes in interpretation from that given by CPV. In the present work the three hydrogen bond distances O–H · · · Br are more nearly alike than in CPV.

In general the agreement between the two independent determinations is gratifying, despite differences in experimental and refinement methods.

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The Crystal Structure of Dicobalt Octacarbonyl*

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The crystal structure of dicobalt octacarbonyl has been determined and refined by two cycles of three-dimensional, isotropic, least-squares calculations. The crystals are monoclinic, space group $P2_1/m$ with $a=6\cdot62$, $b=15\cdot59$, $c=11\cdot31$ Å and $\beta=90°0'\pm20'$. There are two pairs of crystallographically independent molecules per unit cell. The measured density was 1·87 g.cm^{-3}.

The molecular structure of $Co_2(CO)_8$ is very nearly that of $Fe_2(CO)_9$ less one bridge carbonyl group. The consequent lack of trigonal molecular symmetry results in a crystal structure which is a slightly rearranged $Fe_2(CO)_9$ structure.

Introduction

At the time this work was begun, at least six configurations for the dicobalt octacarbonyl molecule had been proposed. The first structure (Syrkin & Dyatkina, 1950) had D_{2h} symmetry and was based purely on theoretical considerations. On the basis of infrared and ultraviolet data (Cable, Nyholm & Sheline, 1954; Friedel, Wender, Shufler & Sternberg, 1955) five additional structures with D_{2h}, C_{2h}, and C_{2v}, D_{3h}, D_{3d} symmetries, respectively, were proposed. Meanwhile Cavalca & Bassi (1953) had reported the results of an incomplete X-ray diffraction study based on a single Patterson projection. In addition to providing cell dimensions, they concluded that the space group was $P2_1$ or $P2_1/m$, and that the molecule was bridged and had the symmetry $2/m$ or mm.

The only binuclear metal carbonyl whose structure had been completely determined at this date was iron enneacarbonyl (Powell & Ewens, 1939). Clearly, dicobalt octacarbonyl needed a thorough investigation to determine its structure, the bridging arrangement, if present, and the extent of the similarity between the $Co_2(CO)_8$ and $Fe_2(CO)_9$ structures. We report here the complete analysis of the structure of $Co_2(CO)_8$ which proves to have the molecular symmetry $C_s=m$, different from any of the six structures previously proposed. A very considerable similarity between the $Co_2(CO)_8$ and the $Fe_2(CO)_9$ structures is demonstrated.

Preliminary investigation

Dicobalt octacarbonyl crystals are orange platelets or laths, best obtained by vacuum sublimation. The crystals must be immediately sealed in capillary tubes or otherwise protected from the air to prevent decomposition. They are biaxial positive. An extinction angle of 23° to [100], which is the direction of elongation, is observed for the (010) platey habit. The unit-cell dimensions found were

$$a=6\cdot62\pm0\cdot03,\ b=15\cdot59\pm0\cdot03\ ,$$
$$c=11\cdot31\pm0\cdot03\ \text{Å};\ \beta=90°\ 0'\pm20'\ ,$$

corresponding to 4 molecules per unit cell. The measured density was 1·87 g.cm^{-3}, while the X-ray density was 1·95 g.cm^{-3}. The systematic absence was $0k0$, k odd; in addition, most of the $hk0$ reflections with h odd were absent. Of the two possible space groups $P2_1$ and $P2_1/m$, the correct one was found to be $P2_1/m$ with a strong pseudo a-glide parallel to (001).

Structure determination

Two-dimensional methods of analysis were largely unsuccessful when applied to this structure. However, it was found that there were two sets of crystallographically independent molecules in the unit cell and that the intramolecular cobalt–cobalt vectors were about 2·54 Å long and parallel to [010], all in agreement with the work of Cavalca & Bassi. Packing considerations showed that some variant of the trigonally arranged bridges of the iron enneacarbonyl structure was more favorable than the bridging arrangements

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[*] This paper is based on the Ph.D. thesis of G. Gardner Sumner.

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