Qualitative agreement between experiment and theory is the principal achievement of this work, but it is also noteworthy that the derived equilibrium constants are acceptably close to previously determined values. Thus for EHDP log K_{11} = 5.60 compares well with the values 6.04,[10] 5.74,[11] and 5.52,[5] and log β_{21} = 9.78 compares well with 9.67.[10] For the higher complexes, it is found that log β_{32} = 20.2 and log β_{74} = 49.4. These values are to be compared with 18.78 and 48.23, respectively.[5] Some differences in the values for the higher complexes are in fact expected because the "core-links" model assumed here is known to be slightly inadequate to describe the full range of species found in Ca^{2+}–EHDP systems.[5] The value for $K_{so}(Ca_2EHDP)$, the most uncertain of the derived quantities, probably errs on the high side because the method of estimation neglects the (presumably) low level of soluble species in equilibrium with the solid.[12]

The value of log $K_{21}(Ca_2P_2O_7)$ = 2.80 compares well with values commonly observed for other 2–2 electrolyte pairs such as $CaSO_4$, *viz.*, log $K_{21} \cong 2.70$,[13] and with the order of magnitude expected based on data for $Mg_2P_2O_7$, for which log K_{21} = 2.33.[14] The value pK_{so} = 12.87 found here compares poorly with pK_{so} = 14.7, previously determined by Wolhoff and Overbeek.[15] This latter value is perhaps too high by at least an order of magnitude, however, since its derivation depends on the authors' value of log K_{11} = 6.8, which is out of the range of accepted values for this quantity. This range is from 4.41 to 5.60 for media of 1.0 ionic strength down to infinite dilution.[16,17]

Conclusions

The most significant result of this work is that a formulation is provided for distinguishing polynucleating from nonpolynucleating systems by precipitation boundary measurements alone. Although aggregate charges are identical with the mononuclear precursor's charge and hence would not be distinguishable from the mononuclear complex in the conventional formalism,[7,18] the present formalism reveals two points of contrast at which systems of the two types can be seen to differ, without placing severe demands on experimental precision.

With respect to the derivation of thermodynamic parameters from the experimental precipitation boundaries the present method is greatly preferred over the method of tangents as employed with AgBr and other compounds.[19] This latter method becomes increasingly imprecise as species existence domains overlap. The present method overcomes this shortcoming by looking at all species effects simultaneously.

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Molecular Structure of Phosphorus Tribromide as Studied by Gas Electron Diffraction and Microwave Spectroscopy

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The internuclear distances and the mean vibrational amplitudes for PBr_3 have been determined by gas electron diffraction: r_g(P–Br) = 2.2204 ± 0.003 Å, r_g(Br–Br) = 3.424 ± 0.006 Å, θ_α(Br–P–Br) = 101.0 ± 0.4°, l(P–Br) = 0.053 ± 0.005 Å, and l(Br–Br) = 0.098 ± 0.007 Å, where the uncertainties represent estimated limits of error. The microwave spectra for $P^{79}Br_3$ and $P^{81}Br_3$ have given the rotational constants, B_0, 1035.24 ± 0.04 and 1010.96 ± 0.04 MHz, respectively, and the centrifugal distortion constant, D_J, $(2.2 \pm 0.9) \times 10^{-4}$ MHz. The average structure for the ground vibrational state, calculated from the r_g distances with corrections for vibrational and centrifugal effects, is consistent with the rotational constants B_z calculated from the above B_0. The experimental D_J constant and mean amplitudes agree with those estimated from the quadratic force constants.

Introduction

The internuclear distances in phosphorus tribromide were first determined by Lister and Sutton[2] to be r(P–Br) = 2.23 ± 0.04 Å and θ(Br–P–Br) = 100 ± 2° by means of the visual method of electron diffraction. Swingle[3] also reported the structure to have r = 2.18 ± 0.03 Å and θ = 101.5 ± 1.5° by the same method. On the other hand, the rotational constants of $P^{79}Br_3$ and $P^{81}Br_3$ measured by microwave spectroscopy[4] gave another set of estimates for the P–Br distance (r_0),

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[1] Microwave spectra were measured by this author at the Government Chemical Industrial Research Institute, Tokyo.

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2.20 ± 0.03 Å, and the bond angle, 106 ± 3°. One notes that the bond angle estimated from spectroscopy is significantly larger than those determined by electron diffraction. The purpose of the present study is to reinvestigate the structure of this molecule by means of the above methods with an accuracy comparable with those of the PF_3[5,6] and PCl_3[7] structures determined in recent studies.

Electron Diffraction

A product of Wako Chemicals Co. was used after distillation. Electron diffraction photographs were taken with an apparatus equipped with an r^3 sector and with the accelerating voltage of about 40 kV.[8] The camera lengths were measured to be 11.235 and 24.747 cm. The scale factor was calibrated by use of the photographs of CO_2 and N_2 taken with the short and long camera lengths, respectively.[5] The sample was led into the apparatus through a high-temperature nozzle[9] (heated to 100°, where the pressure of the sample was about 6 Torr). The optical densities (D = 0.21–0.55) were assumed to be proportional to the electron intensities (Table I) and were analyzed by a standard least-squares method.[10,11] The asymmetry parameter[11] $\varkappa$(P–Br) was estimated[12] to be 5×10^{-6} Å^3, which is larger than the $\varkappa$(P–F) for PF_3[5] by an order of magnitude since the P–Br bond has a much larger mean amplitude of vibration. The $\varkappa$(Br–Br) was assumed to be zero, since the experimental radial distribution peak was found to be practically Gaussian. The elastic and inelastic scattering factors and the phase shifts were taken from the tables prepared by Bonham and his coworkers.[13] No account was taken of the effect of intramolecular and intermolecular multiple scattering.[14]

TABLE I

INTENSITY AND BACKGROUND DATA FOR PBr_3[a]

q	I_t	I_b	q	I_t	I_b	q	I_t	I_b	q	I_t	I_b	q	I_t	I_b
			7	5330		8	5577		9	5341	5549	10	5253	5536
11	5561	5407	12	5914	5186	13	5783	5044	14	5098	4962	15	4320	4829
16	3987	4746	17	4248	4670	18	4762	4611	19	5035	4558	20	4900	4515
21	4541	4479	22	4289	4451	23	4269	4428	24	4382	4411	25	4414	4401
26	4341	4395	27	4263	4393	28	4339	4395	29	4511	4397	30	4631	4397
31	4580	4400	32	4382	4404	33	4197	4406	34	4175	4409	35	4327	4411
36	4504	4417	37	4590	4425	38	4531	4434	39	4454	4444	40	4425	4457
41	4452	4471	42	4478	4488	43	4469	4503	44	4449	4521	45	4472	4540
46	4559	4561	47	4669	4567	48	4715	4597	49	4677	4618	50	4608	4641
51	4564	4663	52	4598	4684	53	4684	4706	54	4759	4729	55	4793	4750
56	4801	4770	57	4806		58	4824		59	4843		60	4854	
21	10275		22	9787		23	9753		24	9787		25	9745	9751
26	9577	9682	27	9417	9612	28	9442	9544	29	9655	9477	30	9820	9420
31	9701	9365	32	9322	9331	33	8945	9297	34	8878	9269	35	9046	9241
36	9354	9220	37	9489	9202	38	9359	9186	39	9192	9177	40	9114	9169
41	9141	9166	42	9142	9161	43	9125	9161	44	8992	9167	45	9061	9185
46	9200	9209	47	9374	9234	48	9470	9264	49	9415	9299	50	9280	9330
51	9205	9362	52	9233	9393	53	9367	9423	54	9498	9453	55	9582	9487
56	9550	9520	57	9582	9551	58	9593	9581	59	9618	9612	60	9623	9643
61	9610	9670	62	9604	9695	63	9676	9718	64	9770	9740	65	9845	9762
66	9884	9782	67	9837	9804	68	9800	9824	69	9771	9844	70	9786	9864
71	9843	9878	72	9910	9891	73	9933	9890	74	9940	9903	75	9939	9901
76	9901	9896	77	9891	9890	78	9855	9882	79	9837	9873	80	9831	9864
81	9836	9855	82	9865	9847	83	9873	9838	84	9875	9825	85	9834	9813
86	9781	9796	87	9730	9776	88	9737	9756	89	9727	9733	90	9712	9717
91	9703	9694	92	9687	9671	93	9662	9645	94	9640	9625	95	9601	9598
96	9568	9570	97	9515	9540	98	9495	9507	99	9462	9473	100	9438	9439
101	9428	9407	102	9379	9373	103	9350	9340	104	9317	9308	105	9262	9273
106	9236	9239	107	9183	9201	108	9169	9163	109	9121	9122	110	9082	9082
111	9050		112	9005		113	8961							

[a] Typical experimental leveled intensity $I_t(q)$ and background $I_b(q)$, defined in ref 11, for long (top) and short (bottom) camera lengths: 24.747 and 11.235 cm. For an exact calibration of the scale factor, the listed q values should be divided by 0.9978 and 1.0022 for long and short camera lengths, respectively.

The observed and best-fit molecular intensities are shown in Figure 1, and the corresponding error matrix is given in Table II. The internuclear distances, their mean amplitudes, and the bond angles, which conform to conventional definitions,[15] are listed in Table III.

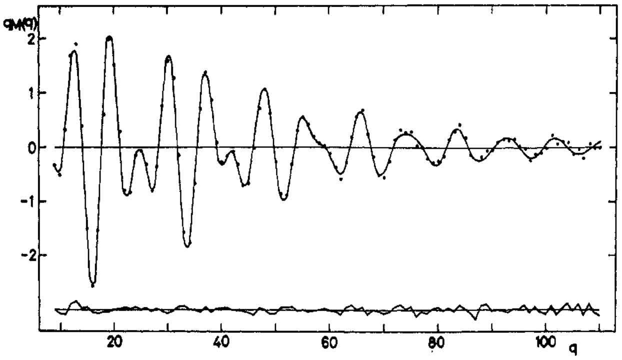

Figure 1—Experimental and best-fit theoretical molecular intensity curve shown in dots and solid curve, respectively. Differences are also shown.

TABLE II

ERROR MATRIX[a]

	r(P–Br)	r(Br–Br)	l(P–Br)	l(Br–Br)	k_1	k_2
r(P–Br)	10	−1	3	3	8	22
r(Br–Br)		13	−5	−3	−7	−27
l(P–Br)			21	12	39	100
l(Br–Br)				13	32	66
k_1					118	197
k_2						581

[a] Elements of the matrix are given by $\sigma_{ij} = \mathrm{sgn}[(B^{-1})_{ij}] \cdot [|(B^{-1})_{ij}| V^*PV/(n - m)]^{1/2}$, where the notations follow ref 10. The units for the distances r_a and the mean amplitudes l are 10^{-4} Å, and those for the indices of resolution (k_1 = 0.949 and k_2 = 0.943) are 10^{-4}. The indices k_1 and k_2 correspond to the molecular intensities obtained from the long (q = 9–56) and short (q = 57–110) camera lengths, respectively.

TABLE III

STRUCTURAL PARAMETERS AND MEAN AMPLITUDES FROM ELECTRON DIFFRACTION[a]

	P–Br, Å	Br–Br, Å	Br–P–Br, deg
r_a	$2.219_0 \pm 0.003$	$3.420_2 \pm 0.006$	
r_g	$2.220_4 \pm 0.003$	$3.423_7 \pm 0.006$	
r_α	$2.216_3 \pm 0.003$	$3.419_6 \pm 0.006$	$100.9_7 \pm 0.4$
$r_\alpha{}^0$ (r_z)	2.2155 ± 0.004	$(3.4178 \pm 0.009)^b$	$100.9_5 \pm 0.3_5)^b$
l_{obsd}	0.053 ± 0.005	0.098 ± 0.007	
l_{calcd}	0.057 ± 0.003	0.109 ± 0.005	

[a] Uncertainties represent estimated limits of error.[5] See ref 15 for the definitions of distances and angles in a molecule exerting vibration and rotation. [b] Estimated from r_z(P–Br) and eq 4. See Discussion.

The experimental errors quoted in Table III are estimated from random and systematic errors.[5] Systematic errors in the distance parameters originate essentially from the uncertainties in the scale factor (less than 0.1%)[5] and in the $\varkappa$ parameters. The changes of $\pm 3 \times 10^{-6}$ Å^3 and $\pm 3 \times 10^{-5}$ Å^3 in $\varkappa$(P–Br) and $\varkappa$(Br–Br), respectively, shift the cor-

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responding r_g distances by $\pm 1 \times 10^{-3}$ Å and $\pm 5 \times 10^{-3}$ Å; the limit of uncertainty in $\varkappa$(Br–Br) given above is estimated from least-squares analyses, where the $\varkappa$(Br–Br) parameters fixed to any value outside this range resulted in significant undulations with a period of about 6 Å^{-1} in the residuals $[qM(q)_{\text{obsd}} - qM(q)_{\text{best fit}}]$ in $q \approx 25$ and $q \approx 75$. Consequently, the error in the angle parameter is mainly determined by the systematic error in $\varkappa$(Br–Br). Molecular intensities measured with the short (S) and long (L) camera lengths were found to have different indices of resolution in the overlapping region (q = 25–56), about 0.80 for S and 0.95 for L. Since this systematic discrepancy was ascribed to the extraneous scattering in the S intensity in this region and since the mean amplitudes had strong correlation with the index of resolution (see Table II), the L intensity was taken for $q \leq 56$. The index of resolution of the S intensity for $q \geq 57$ was 0.94. The systematic errors in the amplitudes from the correlation with the index of resolution were estimated to be of the order of their random standard errors. As a test of the influence of scattering factors on the amplitudes, the scattering factors reported by Bonham and Strand[16] were also used for the analysis. The changes in the indices of resolution and the P–Br and Br–Br amplitudes were 0.02, −0.005 Å, and 0.003 Å, respectively, whereas no influence on the distance parameters was observed.

The theoretical amplitudes given in Table III were calculated from the F matrices estimated in the following procedure. Off-diagonal elements, F_{12} and F_{34}, of the two-dimensional F matrices for the A_1 and E species were estimated in the scheme of the Urey–Bradley force field[17] to be 0.110 and −0.055 mdyn/Å, respectively; the force constants representing nonbonded interaction, F(Br–Br) = 0.1186 mdyn/Å and F'(Br–Br) = −0.0067 mdyn/Å, were estimated by taking derivatives of the Lennard-Jones potential of a krypton–krypton atom pair[18]

$$\varphi(r) = \epsilon[(r_{\text{m}}/r)^{12} - 2(r_{\text{m}}/r)^6] \qquad (1)$$

with $r_{\text{m}} = 4.04$ Å and $\epsilon/k = 159$°K, placed at the Br–Br distance (r = 3.420 Å). The diagonal elements were then determined by the use of the vibrational frequencies[19] (ν_1 380, ν_2 162, ν_3 400, ν_4 115 cm^{-1}) to be $F_{11} = 2.179$, $F_{22} = 0.300$, $F_{33} = 1.791$, and $F_{44} = 0.199$ mdyn/Å. The errors in the calculated mean amplitudes, given in Table III, were estimated by assuming the uncertainties in the frequencies to be 15 cm^{-1} for ν_1 and ν_3 and 5 cm^{-1} for ν_2 and ν_4 and the uncertainties in F_{12} and F_{34} estimated above to be equal to their absolute values.

Thus the experimental and calculated values of the mean amplitudes agree with each other within the range of their limits of error.

Microwave Spectroscopy

The rotational spectrum was recorded at room temperature with a conventional microwave spectrometer with 100-kHz Stark modulation of 150-V square waves. The half-widths of the lines were about 3 MHz, and no splitting due to the hyperfine structures of the bromine quadrupole interactions was observed. Six transitions for $P^{79}Br_3$ and five for $P^{81}Br_3$ in the ground vibrational state, listed in Table IV, were assigned. Several absorption lines for mixed isotope species $P^{79}Br_2{}^{81}Br$ and $P^{79}Br^{81}Br_2$ were observed in the expected regions, but they were not analyzed since the spectra were complicated by the presence of other lines for molecules in excited vibrational states.

TABLE IV

OBSERVED TRANSITION FREQUENCIES, ROTATIONAL CONSTANTS B_0, AND CENTRIFUGAL CONSTANTS D_J (IN MHz)[a]

J	$P^{79}Br_3$ Obsd	$P^{79}Br_3$ Obsd − calcd	$P^{81}Br_3$ Obsd	$P^{81}Br_3$ Obsd − calcd
12 ← 11	$24,843.9_6$	-0.1_8		
13 ← 12	$26,913.8_6$	-0.3_4	$26,283.4_0$	0.4_0
14 ← 13	$28,984.3_4$	0.1_4	$28,304.3_4$	-0.1_0
15 ← 14	$31,054.1_0$	-0.0_1	$30,325.9_0$	0.1_0
16 ← 15	$33,124.0_2$	0.2_7	$32,347.2_0$	0.1_2
17 ← 16	$35,193.9_8$	0.2_8	$34,367.8_0$	-0.4_8
	$B_0 = 1035.24 \pm 0.04$		$B_0 = 1010.96 \pm 0.04$	

$D_J = (2.2 \pm 0.9) \times 10^{-4}$

$D_J(\text{calcd})^b = (2.3 \pm 0.2) \times 10^{-4}$

[a] Uncertainties represent 2.5 times random standard errors.
[b] Calculated by the use of eq 3 with estimated force constants.

Since the shapes of the absorption lines were symmetric on right and left, the transition frequencies were fitted to the formula

$$\nu_{J+1\leftarrow J} = 2B_0(J+1) - 4D_J(J+1)^3 \qquad (2)$$

where the parameters D_J for $P^{79}Br_3$ and $P^{81}Br_3$ were assumed to be equal, and the effect of D_{JK} was ignored. The D_J parameter thus determined, shown in Table IV, is consistent with the D_J(calcd) calculated by the use of the force constants estimated above and a theoretical formula[20]

$$\begin{aligned} D_J = B_{\text{e}}^3[&4(1 - B_{\text{e}}/2C_{\text{e}})(\beta_1^2/\omega_1^2 + \beta_2^2/\omega_2^2) + \\ &4\beta_1\beta_2(B_{\text{e}}/C_{\text{e}})^{1/2}(1 - B_{\text{e}}/2C_{\text{e}})^{1/2}(1/\omega_2^2 - 1/\omega_1^2) + \\ &(B_{\text{e}}/C_{\text{e}})(\beta_2^2/\omega_1^2 + \beta_1^2/\omega_2^2 + \delta_4^2/\omega_3^2 + \\ &\delta_3^2/\omega_4^2)] \end{aligned} \qquad (3)$$

where the notations follow ref 21.

According to the effective moments of inertia reported in ref 4, $I_0(P^{79}Br_3) = 841.9 \times 10^{-40}$ g cm^2 and $I_0(P^{81}Br_3) = 860.9 \times 10^{-40}$ g cm^2, four absorption lines should have been present in the range 28,600–32,500 MHz (*e.g.*, 29,244 MHz for $P^{81}Br_3$, J = 15 ← 14), but no absorption lines with an intensity higher than 1×10^{-9} cm^{-1} were observed near the predicted frequency regions.

Discussion

With corrections for vibration–rotation interactions[15,22] on the effective rotational constants B_0 determined above, the average rotational constants B_z are calculated to be 1034.1_5 and 1009.9_2 MHz for $P^{79}Br_3$ and $P^{81}Br_3$, respectively. They represent approximately linear relations, which are almost identical with each other, between the r_z(P–Br) (Å) and θ_z(Br–P–Br)

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(deg) parameters

$$\theta_z = 100.99 - 86.5(r_z - 2.215) \qquad (4)$$

On the other hand, since the r_z(P–Br) is estimated to be 2.2155 ± 0.004 Å from the electron diffraction $r_\alpha{}^0$ parameter given in Table III, the θ_z angle is calculated to be 100.95 ± 0.35°. Accordingly, θ_z (the angle defined with reference to the average nuclear positions *for the ground vibrational state*) is nearly equal to the θ_α (the angle defined with reference to the *temperature-averaged* nuclear positions) given in Table III (100.98 ± 0.4°). In other words, the θ_α angle appears to be almost temperature independent, in spite of the relatively low frequencies[19] of bending vibrations. A similar remark has previously been made by one of the authors.[5,23]

The observed bond angle is shown to be the largest among those in the phosphorus trihalides listed in Table V.

TABLE V

STRUCTURE OF PHOSPHORUS TRIHALIDES

	r_g(P–X), Å	θ_α(X–P–X), deg	Ref
PF_3	1.570 ± 0.0012	97.8 ± 0.2	5
PCl_3	2.040 ± 0.0014	100.27 ± 0.09	7
PBr_3	2.220 ± 0.003	101.0 ± 0.4	Present study

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The Crystal Structure of Cesium 3,3′-*commo*-Bis[nonahydro-1,2-dimethyl-1,2-dicarba-3-chroma-*closo*-dodecaborate] Hydrate, a Hydrate of a Chromium Metallocarborane Salt[1]

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The crystal structure of the monohydrated cesium salt of $Cr[B_9C_2H_9(CH_3)_2]_2^-$, 3,3′-*commo*-bis[nonahydro-1,2-dimethyl-1,2-dicarba-3-chroma-*closo*-dodecaborate](1−), has been determined by X-ray diffraction. The crystals are tetragonal, space group $P4_12_12$ (or $P4_32_12$), with $a = 9.938 \pm 0.004$ Å and $c = 22.739 \pm 0.007$ Å. With four molecules of $CsCr[B_9C_2H_9(CH_3)_2]_2 \cdot H_2O$ in the unit cell the density is calculated to be 1.55 g/cm³. The model was refined by least squares to a conventional R of 0.047 for 1957 point group independent reflections, measured with a scintillation counter (θ–2θ scan). The metallocarborane anion consists of two icosahedra sharing a chromium atom as common vertex. Each icosahedron is composed of the chromium atom, nine boron atoms each bonded to a terminal hydrogen atom, and two carbon atoms each bonded to a methyl group. The carbon atoms in the cage are bonded to each other and to the chromium atom. The pair of methyl groups on one cage are rotated as far as possible from those on the other. The shape of the anion corresponds closely to symmetry $2/m$. Average bond distances are Cr–C = 2.27, Cr–B = 2.26, C–C(methyl) = 1.52, C–C(cage) = 1.64, C–B = 1.72, and B–B = 1.77 Å.

Introduction

Ruhle and Hawthorne have recently reported[2] the preparation of $Cr[B_9C_2H_9(CH_3)_2]_2^-$, another in the series of transition metal derivatives of the dicarbollide ion, $B_9C_2H_{11}^{2-}$. In this anion, 3,3′-*commo*-bis[nonahydro-1,2-dimethyl-1,2-dicarba-3-chroma-*closo*-dodecaborate](1−),[3] the chromium is in a formal 3+ valence state and is bonded to two icosahedral dicarbollide ions in which the hydrogen atoms on the carbons of $B_9C_2H_{11}^{2-}$ have been replaced by methyl groups. It was expected that the complex would have a sandwich-type structure in which the chromium would simultaneously occupy an apex in each of two icosahedra.

The crystal structure determination of the monohydrate of the cesium salt of the metallocarborane anion, $CsCr[B_9C_2H_9(CH_3)_2]_2 \cdot H_2O$, is reported here. The sandwich nature of the anion structure, shown in Figure 1, is confirmed and it is shown that the cages are staggered across the chromium with the carbon atoms of one cage rotated as far as possible from those in the other.

Experimental Section

The dark red crystals of $CsCr[B_9C_2H_9(CH_3)_2]_2 \cdot H_2O$ were well-formed square prisms elongated along [001]. The largest faces were (110). The crystal used for the final intensity measurements was a prism 0.10 × 0.10 mm in cross section and was cut parallel to (001) to a thickness of 0.09 mm. It was glued to the tip of a glass fiber with [001] as the rotation axis.

After preliminary examination by photographic methods, the space group absences were checked and more accurate cell dimensions were obtained from measurements on the $h00$, $0k0$, and $00l$ reflections with a manually operated General Electric diffractometer using copper radiation (Cu Kα_1; λ 1.5405 Å). A card-controlled General Electric diffractometer equipped with a quarter-circle, Eulerian-cradle goniostat was used for collecting intensity data. Copper Kα radiation filtered with 0.003 in. of

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.*, **7**, 2279 (1968).

[3] This name comes from the American Chemical Society approved nomenclature rules: *ibid.*, **7**, 1945 (1968). The name given by Ruhle and Hawthorne in ref 2 is bis[π-(3)-1,2-dimethyl-1,2-dicarbollyl]chromium(III).