Short Communications

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Single crystals of BaAl₂O₄. By R. H. ARLETT, J. G. WHITE, and M. ROBBINS, RCA *Laboratories, Princeton, New Jersey, U.S.A.*

$BaAl_2O_4$ single crystals are hexagonal with $a = 10.444 \pm 0.002$, $c = 8.793 \pm 0.002$ Å, the a axis being doubled compared with the previously reported value.

Single crystals of $BaAl_2O_4$ were grown from a barium borate flux. The starting materials were melted in a platinum crucible which was heated to 1275°C in a globar furnace. The crystals were grown by slow cooling of the melt at a rate of 2°C per hour. Single crystals grew in the shape of clear hexagonal rods (3 mm long × 0·5 mm diameter) parallel to the c axis and bounded by $\{10\bar{1}0\}$ and $\{0001\}$ faces.

Single-crystal X-ray photographs showed very weak additional reflections which required a doubling of the hexagonal a axis compared with the unit cell reported by previous workers on polycrystalline material (Wallmark & Westgren, 1937; Do Dinh & Bertaut, 1965)*. A similar doubling of the a axis in this structure type has been found in single crystals of $BaGa_2O_4$ (Hoppe & Schepers, 1960). Lattice constants $a = 10.444 \pm 0.002$ Å, $c = 8.793 \pm 0.002$ Å

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* These authors reported space group $P6_322$. The structure is described (*Strukturbericht*, 1937) as type $H2_8$.

were obtained by a least-squares fit of the back reflection powder diffraction lines.

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The crystal structure of diaquobis(acetylacetonato)magnesium(II).* By B. MOROSIN, *Sandia Corporation, Albuquerque, New Mexico, U.S.A.*

The crystal structure of diaquobis(acetylacetonato)-magnesium(II), $Mg(C_5H_7O_2)_2 . 2H_2O$, has been determined. The coordination polyhedron about the magnesium atom is tetragonally distorted (2.03, 2.04 and 2.15 Å) to a similar degree to that found in the corresponding isomorphous nickel and cobalt compounds. This suggests that the tetragonal distortion is due to a crystal structure (or packing) effect rather than the electronic structure of the metal ions. A tabulation of metal ion displacements from the least-squares plane formed by the atoms of the chelate ring in metal acetylacetonates is given.

Bullen (1959) and Montgomery & Lingafelter (1964) have reported the crystal structures of diaquobis(acetylacetonato)-cobalt(II) and -nickel(II) ($MQ_2.2H_2O$ where M = Co or Ni and $Q = C_5H_7O_2$, respectively). In both compounds, the metal ion is surrounded by six oxygen atoms which form a tetragonally distorted octahedron. Covalent bonding involving hybridization with d orbitals or, in terms of

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ligand-field theory, asymmetric $d\gamma$ and $d\varepsilon$ subshells have been invoked to explain the tetragonal distortion. It has been suggested (Bullen, 1959) that the zinc analog, with a more symmetric electronic structure, should exhibit a more regular octahedral environment about the metal ion; however, the only reported zinc complex (Montgomery & Lingafelter, 1963) is a monohydrate in which the zinc ion is not octahedrally coordinated. We present here our structure results on $MgQ_2.2H_2O$ which show the environment about the magnesium ion to be tetragonally distorted and,

therefore, appear to contradict the electronic explanation proposed by Bullen. We also present crystallographic data on two other magnesium acetylacetonate compounds: the anhydrous material and a triclinic hydrate.

The lattice constants for $MgQ_2.2H_2O$ are $a_0 = 10.9836$ (16), $b_0 = 5.3537(12)$, $c_0 = 11.1761(10)$ Å and $\beta = 106.356$ (14)°. These values were obtained by least-squares fit of 66 high 2θ reflections from Cu $K\alpha$ (λ for $K\alpha_1 = 1.54050$ Å) Weissenberg photographs standardized by superimposing $PbNO_3$ powder lines ($a_0 = 7.8543$ Å). There are two molecules in the cell of symmetry $P2_1/c$.

Crystals of another hydrate are also easily obtained. These thin plates are easily bent and usually twinned. They belong to the triclinic system with lattice constants $a_0 = 7.89(8)$, $b_0 = 11.08(9)$, $c_0 = 9.04(8)$ Å, $\alpha = 104.2(3)$, $\beta = 90.3(3)$, $\gamma = 98.5(3)°$ and do not appear to be isomorphous with any of the hydrates of bisacetylacetonatocobalt(II) reported by

Cotton & Elder (1966). However, powder patterns attributed to bisacetylacetonate dihydrates (Holm & Cotton, 1961; Morosin, 1964) have contained interplanar spacings which can be indexed only with a combination of the two compounds (Table 1). We have recently discovered that Montgomery (1960) had isolated the corresponding nickel compound with lattice constants $a_0 = 7.58(1)$, $b_0 = 11.03(2)$, $c_0 = 9.10(2)$ Å, $\alpha = 105.9(2)$, $\beta = 90.0(1)$, and $\gamma = 92.1(2)°$.

Upon dehydration, MgQ_2 yields a powder pattern similar to that of NiQ_2 and probably forms molecules which are trimeric, similar to those reported by Bullen (1956) for the nickel compound. Table 2 lists interplanar spacings observed for the anhydrous magnesium compound together with the calculated values for the nickel compound ($a_0 = 15.65$, $b_0 = 23.23$, $c_0 = 9.64$ Å in space group $Pmab$).

Three-dimensional Mo $K\alpha$ intensity data were collected on two different $MgQ_2.2H_2O$ crystals (both very thin) with

Table 1. *Interplanar spacings for metal bisacetylacetonate hydrates*

$NiQ_2.2H_2O*$	$CoQ_2.2H_2O*$	$MgQ_2.2H_2O†$	$MgQ_2.xH_2O†$	Calc. $A‡$	Calc. $B§$
11.5m	11.4m				
10.3s	10.5vs	10.5vs	10.7vvs	10.5 (100)	10.6 (010)
	8.70w		8.75m		8.75 (001)
			7.80w		7.80 (100) 7.77 (01$\bar{1}$)
5.92w	5.87m		5.88s		5.95 (10$\bar{1}$)
			5.67m		5.70 (101)
5.38vs	5.40vs	5.42s		5.44 (10$\bar{2}$)	
		5.37s	5.30vvw	5.36 (002)	
		5.24vw		5.26 (200)	5.31 (020)
5.02vw	5.04vw				5.14 (02$\bar{1}$) 4.91 ($\bar{1}$11)
4.77vs	4.80s	4.78s		4.79 (011) 4.77 (110)	
4.55vs	4.58s	4.58m		4.58 (11$\bar{1}$)	
		4.40vvw	4.45vvwB	4.43 (20$\bar{2}$)	4.47 (1$\bar{2}$0) 4.46 (01$\bar{2}$)
4.29w	4.28vw	4.30vvw		4.31 (102)	4.27 (12$\bar{1}$)
4.15m	4.19m	4.16w	4.20vvwB	4.17 (111)	4.11 (021)
		3.83vvw	3.80vvw	3.82 (11$\bar{2}$)	3.82 (1$\bar{1}$2)
3.79s	3.79vs	3.78s	3.78s	3.79 (21$\bar{1}$) (012)	3.74 (012) (102)
			3.70vvw	3.76 (210)	3.71 (121) (2$\bar{1}$0)
3.46m	3.48m	3.50w	3.50w	3.51 (300)	3.50 (201) (21$\bar{1}$) (12$\bar{2}$)
3.41s	3.42s	3.40s	3.30−3.42vwB	3.42 (21$\bar{2}$) 3.41 (30$\bar{2}$)	3.30 3.43−($\bar{1}$12) ($\bar{2}$11) (112) (1$\bar{3}$1) (130)
				3.36 (112)	
3.34w	3.35w	3.34w		3.34 (211)	
		3.32w		3.32 (202)	
3.05s	3.06s	3.04m		3.05 (11$\bar{3}$)	
				3.02 (31$\bar{1}$)	
			2.98w	2.97 (013)	2.98 (20$\bar{2}$) (21$\bar{2}$)
2.97s	2.98s	2.97m		2.97 (310)	
			2.93w	2.90 (21$\bar{3}$)	2.93 (1$\bar{3}$2) (13$\bar{2}$)
2.87vw	2.86vw	2.88w		2.88 (31$\bar{2}$)	
2.79w	2.80w	2.81w		2.82 (212)	
		2.78w		2.79 (10$\bar{4}$)	
			2.72vvw	2.72 (20$\bar{4}$)	2.72 (2$\bar{2}$2) (04$\bar{1}$) (12$\bar{3}$) (103)
				2.70 (113)	
2.65m	2.67m	2.67m		2.68 (402) (004) (020) (311)	
				2.63 (400)	
				2.62 (302)	
			2.60w	2.60 (021)	2.60 (1$\bar{4}$1) (300) (03$\bar{3}$)
2.58mw	2.58m	2.58w		2.59 (120) (31$\bar{3}$)	
		2.56w		2.56 (12$\bar{1}$)	

* Reported by Holm & Cotton (1961). Values at higher scattering angles omitted here.
† Powder pattern from mechanically (microscopic) separated crystals (this work).
‡ Calculated from monoclinic lattice constants (see text).
§ Calculated from triclinic lattice constants (see text); only observed spacings listed.

Table 2. *Interplanar spacings observed for anhydrous bis(acetylacetonato)magnesium*(II).*

MgQ_2	d spacings calculated from Bullen (1956)
	11·6 (020)
9·65*m*	9·64 (C01)
9·20*s*	9·33 (121)
	8·90 (011), 7·83 (200)
7·73*m*	7·74 (111)
7·45*m*	7·42 (021)
	6·70 (121), 6·49 (220)
6·10*w*	6·08 (201)
5·95*w*	6·04 (031)
5·70*vw*	5·88 (211), 5·81 (040)
5·45*vw*	5·63 (131), 5·44 (140)
5·18*vw*	5·38 (221)
4·98*w*	4·97 (041)
4·80*w*	4·82 (002), 4·78 (231), 4·76 (320)
	4·74 (141), 4·72 (012)
4·58*w*	4·66 (240), 4·52 (112), 4·50 (311)
	4·45 (022), 4·28 (122), 4·27 (321)
4·20 *w*	4·19 (241) (051)
4·13*vw*	4·10 (202)
4·07*vw*	4·09 (032)
4·02*vw*	4·04 (151) (212)
	3·95 (132) (331), 3·91 (400)
3·87*vw*	3·88 (340), 3·87 (060) (222)
3·72*w*	3·76 (160), 3·71 (042) (420), 3·69 (251)
3·60*vw*	3·63 (232) (401), 3·61 (142), 3·60 (341), 3·59 (061) (411)
3·52*w*	3·50 (161) (312)
3·43*vw*	3·47 (260), 3·46 (421)
3·40*w*	3·38 (322), 3·35 (242) (052)

* Values observed and calculated arbitrarily omitted for d spaces smaller than 3·35.

Table 3. *Final atomic coordinates*

		x	y	z
Mg		0·0	0·0	0·0
O(1)		0·1470 (2)	0·2196 (6)	0·0957 (2)
O(2)		0·1170 (2)	−0·1591 (6)	−0·0898 (3)
O(3)		0·0541 (3)	−0·2869 (6)	0·1392 (3)
C(1)		0·3576 (4)	0·3371 (11)	0·2004 (4)
C(2)		0·2636 (4)	0·1738 (9)	0·1105 (3)
C(3)		0·3093 (4)	−0·0156 (10)	0·0478 (4)
C(4)		0·2368 (4)	−0·1678 (9)	−0·0463 (3)
C(5)		0·3026 (5)	−0·3648 (10)	−0·1032 (4)
H(1)		0·35	−0·03	0·67
H(2)	C(1)	0·33	0·12	0·78
H(3)		0·44	0·20	0·72
H(4)		0·715	0·12	0·695
H(5)	C(5)	0·75	−0·03	0·59
H(6)		0·61	0·14	0·575
H(7)	C(3)	0·41	−0·02	0·80
H(8)	O(3)	0·93	0·48	0·86
H(9)		0·94	0·24	0·78

a Datex automatic system to drive the Picker diffractometer. Two sets each of scanned and of balanced-filter peak height data for each crystal as well as one set from one crystal of balanced-filter scanned data were collected and placed on a common scale using the 'standard' set of reflections monitored for crystal and alignment stability. Plots of ratios (between sets of data) of groups of the stronger Bragg reflections *versus* scattering angle were linear to 40° in 2θ. A few reflections along strong lattice rows were consistently stronger ($\sim 10\%$) in the scanned data than in the peak height data. Because the crystals were thin and thus many of the reflections were of low value, no further analyses on different sets of data were carried out. The intensity data were averaged and used for least-squares refinement (the function, $\Sigma w(F_o - F_c)^2$, was minimized; weights, w, were calculated from counting statistics) of positional and thermal parameters.

The final atomic coordinates and anisotropic thermal parameters are given in Tables 3 and 4. Hydrogen positions

Table 4. *Anisotropic temperature factors* B_{ij}

The temperature factor is of the form $\exp\left(-\frac{1}{4} \sum_{i=1}^{3} \sum_{j=1}^{3} B_{ij} h_i h_j a_i^* a_j^*\right)$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mg	2·10 (7)	2·90 (9)	1·81 (7)	−0·04 (8)	0·62 (6)	−0·38 (8)
O(1)	2·05 (10)	3·27 (15)	2·25 (11)	0·14 (11)	0·44 (9)	−0·49 (12)
O(2)	2·07 (10)	3·96 (16)	2·14 (11)	0·15 (11)	0·61 (9)	−0·70 (12)
O(3)	4·01 (14)	3·16 (16)	2·33 (12)	0·24 (13)	0·55 (11)	−0·00 (12)
C(1)	2·65 (16)	4·50 (26)	2·88 (18)	−0·68 (19)	0·54 (15)	−0·37 (18)
C(2)	2·63 (19)	3·26 (23)	1·46 (15)	−0·42 (16)	0·50 (14)	0·23 (16)
C(3)	2·19 (16)	3·56 (21)	2·34 (17)	0·40 (19)	0·44 (14)	0·27 (20)
C(4)	3·39 (20)	2·74 (21)	1·43 (15)	0·16 (17)	0·87 (15)	0·27 (16)
C(5)	3·87 (19)	4·22 (24)	2·66 (17)	1·08 (20)	1·47 (17)	−0·20 (19)

Table 5. Observed and calculated structure factors

Asterisks denote 'less than'

were obtained from a difference synthesis (R was 0·096 at this stage) and were not refined in subsequent least-squares cycles. An isotropic thermal parameter equal to 4·0 was assigned to the hydrogen atoms. Final values for observed and calculated structure factors (neutral scattering factors from *International Tables for X-ray Crystallography*; the reliability index, R, is 0·059) are listed in Table 5. Bond lengths and angles are given in Fig. 1.

The structure of MgQ₂.2H₂O is essentially the same as that reported for the corresponding cobalt and nickel compounds. Even though the magnesium ion has a symmetric distribution of electrons and no available d orbitals, its coordination polyhedron is tetragonally distorted (2·03, 2·04, and 2·15 Å) to a similar degree to that found in the corresponding isomorphous nickel (2·01, 2·02, and 2·14 Å) and cobalt (2·05, 2·06 and 2·23 Å) compounds. These results appear to contradict the electronic explanation proposed by Bullen. One would expect the Mg–O separations to be more

like those found in diaquobis(salicylaldehydato)nickel(II) (Stewart, Lingafelter & Breazeale, 1961) with M–O(Q) separations of 2·02 Å and an M–O(H₂O) distance of 2·04 Å. If one were to invoke charge transfer as a mechanism to move the water molecules further away from the metal ions, then one would expect the M–O(Q) separations to be shorter than 2·0 Å (similar to the 1·8–1·9 Å separations found in salicylaldimine complexes; Lingafelter & Braun, 1966). Hence one may conclude that the appearance of the tetragonal distortion in all three MQ₂.2H₂O compounds suggests a crystal structure (or packing) effect.

The magnesium atom is displaced 0·48 Å from the least-squares plane formed by the five atoms of the acetylacetone ring. This displacement is among the largest which has been reported (Table 6) and is exceeded only by those found in ZrQ₄ (Silverton & Hoard, 1963). In complexes containing more than one crystallographically independent ring, we attempted to correlate the small differences in M–O dis-

Table 6. *Distance of metal from ideal ligand plane*

Compound (Q = C₅H₁₇O₂)	Metal	A	B	σ*	Reference
MgQ₂.2H₂O	0·48	0·10	0·19	0·02	This work
CoQ₂.2H₂O	0·41	0·03	0·19	0·02	Bullen (1959)
NiQ₂.2H₂O	0·35	0·07	0·14	0·02	Montgomery & Lingafelter (1964)
ZnQ₂.H₂O	0·29	0·03	0·16	0·02	Montgomery & Lingafelter (1963)
	0·38	0·05	0·09	0·02	
CuQ₂	0·19	0·02	0·04	0·01	Dahl (1966)
AlQ₃	0·13	0·02	0·06	0·002	Pfluger (1964)
	0·16	0·03	0·14	0·03	
	0·13	0·06	0·07	0·002	
CoQ₃	0·13	0·03	0·07	0·02	Pfluger (1964)
	0·14	0·01	0·13	0·003	
	0·11	0·01	0·07	0·004	
CrQ₃	0·12	0·01	0·08	0·02	Morosin (1965)
	0·19	0·01	0·15	0·02	
	0·11	0·01	0·09	0·01	
FeQ₃	0·03	0·02	0·04	0·02	Iball & Morgan (1964)
	0·27	0·09	0·19	0·01	
	0·08	0·08	0·13	0·03	
MnQ₃†	0·12	0·02	0·13	0·01	Morosin & Brathovde (1964)
	0·13	0·03	0·10	0·02	
	0·12	0·02	0·08	0·003	
RhQ₃	0·13	0·02	0·12	0·03	Morrow (1964)
	0·01	0·06	0·14	0·02	
	0·16	0·08	0·11	0·03	
CeQ₄	0·43	0·03	0·23	0·06	Matković & Grdenić (1963)
	0·28	0·03	0·09	0·05	
	0·03	0·00	0·11	0·02	
	0·01	0·02	0·17	0·03	
ZrQ₄	0·70	0·08	0·11	0·02	Silverton & Hoard (1963)
	0·65	0·16	0·21	0·03	
VOQ₂	0·38	0·02	0·23	0·02	Dodge, Templeton & Zalkin (1961)
	0·30	0·03	0·08	0·01	
[CoQ₂]₄	0·25	0·00	0·13	0·04	Cotton & Elder (1965)
	0·29	0·02	0·11	0·03‡	
	0·29	0·12	0·24	0·06‡	
	0·47	0·15	0·32	0·03‡	
[CoQ₂.H₂O]₂	0·26	0·14	0·22	0·02	Cotton & Elder (1966)
	0·24	0·06	0·10	0·02	
	0·14	0·12	0·14	0·02‡	
	0·16	0·03	0·08	0·02‡	
Average	0·24	0·04	0·13	0·02	

* The standard deviation of the atoms (those defining the plane) from the least-squares plane.
† Cell dimensions used are $a_0 = 14\cdot052$, $b_0 = 7\cdot618$, $c_0 = 16\cdot442$ Å, $\beta = 99\cdot39°$.
‡ Oxygen atoms of these rings serve as bridges in forming dimer and tetramer molecules.

tances found in different rings with the displacement of the metal from the least-squares plane, but no systematic effects were found. During our tabulation of metal displacements from the least-squares plane, we noted that one of the methyl carbon atoms (B) is systematically displaced from the plane considerably more than the other (average of 40 rings: 0·13 and 0·04 Å, respectively). This methyl carbon atom (B) is greater than 3σ away from the ideal plane in 38 rings whereas the other (A) is displaced greater than 3σ in only 9 rings. Since the Q residue is inherently symmetrical, steric effects of crystal packing may be responsible. Such reasoning had been given for displacements of methyl carbon atoms and for differences in C (ring) – C (methyl) separations in MnQ_3 (Morosin & Brathovde, 1964). Furthermore, trends may be seen upon examination of members of isomorphous sets in Table 6. In $MQ_2.2H_2O$ all A methyl carbon atoms are crystallographically identical. In MQ_3 (except for Fe which does not belong to the series) the A methyl carbon atoms for the first two entries (rings) of each member are crystallographically equivalent; for the third entry, an interchange (B for A) is involved for Rh and Al. However, from a careful examination of intermolecular separations (ignoring hydrogen positions), one would not have been able to predict the larger displacement for methyl carbon atom B compared with A for the second entry of the members in the MQ_3 series. Perhaps accurate hydrogen positions as well as a knowledge of the intra- and intermolecular forces would be needed.

This compound should be useful as a diamagnetic host for EPR and spectral studies on paramagnetic ions in a tetragonal field.

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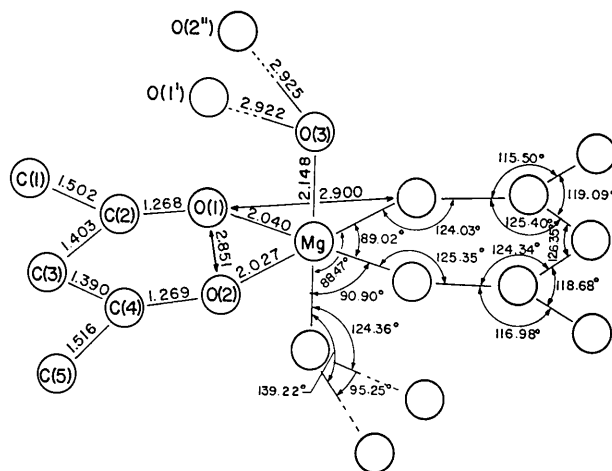

Fig. 1. Bond separations and angles in diaquobis(acetylacetonato)magnesium. The molecules of the complex are linked together by weak (long) hydrogen bonds (2·925 and 2·922 Å) to two different molecules [O(1') and O(2'') are not located about identical metal atoms].

Hydrogen atoms (positions from a Fourier synthesis and not refined) are located 0·92 and 1·04 Å from O(3) (angle formed, 107·9°), 1·06 Å from C(3), 0·89, 1·04, and 1·07 Å from C(1) and 0·93, 0·99 and 1·08 Å from C(5).

The standard deviations of Mg–O, O–O, O–C and C–C separations are 0·004, 0·006, 0·009, and 0·011 Å respectively and of O–Mg–O, Mg–O–C, O–C–C, and C–C–C angles, 0·2, 0·4, 0·7, and 0·8° respectively.

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