

Magnesium Formate–Urea (1/2)*

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(Received 30 April 1991; accepted 14 October 1991)

Abstract. $\text{Mg}(\text{HCO}_2)_2 \cdot 2(\text{NH}_2)_2\text{CO}$, $[\text{Mg}(\text{CHO}_2)_2 \cdot (\text{CH}_4\text{N}_2\text{O})_2]$, $M_r = 234.48$, monoclinic, $C2/c$, $a = 17.094$ (2), $b = 16.842$ (1), $c = 15.198$ (2) Å, $\beta = 123.00$ (1)°, $V = 3669.6$ (6) Å³, $Z = 16$, $D_m = 1.69$, $D_x = 1.686$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 19.26$ cm⁻¹, $F(000) = 1952$, $T = 295$ K, $R = 0.034$ for 3351 reflections. The crystal consists of a quasi-square Mg network connected by HCO₂, which is similar to the A-site lattice in $\text{Mg}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$. Urea molecules are sandwiched between neighbouring $[\text{Mg}(\text{HCO}_2)_2]_\infty$ layers.

Introduction. The field of two-dimensional (2D) antiferromagnetism (AF) is growing rapidly in connection with the mechanism of oxide superconductors and quantum effects in low-dimensional systems. 2D AF materials with an exchange interaction of the order of 1 K are useful because many experimental techniques are rather readily applicable. For example: (1) we do not need ultra low temperature or an extremely high magnetic field for the study of magnetic transition and (2) we can compare our specific heat and/or susceptibility data with theoretical values without large corrections due to the lattice specific heat and/or the diamagnetic susceptibility. Divalent-metal (Mg, Mn, Fe, Co, Ni, Zn and Cd) formate di-ureas, including the title compound, were prepared (Yamagata, Saito, Abe & Hashimoto, 1989) with the aim of obtaining such crystals.

The thermal and magnetic properties of Mn and Co formate di-ureas indicate that they have a 2D magnetic lattice with an exchange of the order of 1 K and do not contain the extralayer magnetic ions seen

in corresponding dihydrates (Takeda, Deguchi, Hoshiko & Yamagata, 1989; Deguchi, Hoshiko, Takeda & Yamagata, 1990). The structure analysis of di-ureas is, therefore, very interesting. In this paper we report the structure determination of the Mg salt as it was the first of seven to be completed. The structures of the Mn, Co, Zn and Cd salts are similar to that of the Mg salt.

Experimental. Crystals were obtained by keeping a very slightly oversaturated aqueous solution at constant temperature (323 K) for several weeks (Yamagata, Saito, Abe & Hashimoto, 1990). Density by pycnometry. A spherical specimen with diameter 0.20 mm, data collected on a Rigaku AFC-5R diffractometer, graphite monochromator. θ - 2θ scan.

The title compound shows Laue class $2/m$. Evidence for the inversion symmetry was obtained from the Wilson plot and from Weissenberg and oscillation photographs. The systematic extinctions (for hkl reflections only $h + k = 2n$ and for $h0l$ only $l = 2n$ appear) gave the centrosymmetric monoclinic space group $C2/c$. Cell dimensions from 30 θ angles ($45 < |\theta| < 75^\circ$).

Five standard reflections measured at regular intervals, no systematic variation observed. Lorentz and polarization corrections. No absorption correction was made because μr (= 0.19) is sufficiently small. $(\sin\theta)/\lambda < 0.638$ Å⁻¹ ($0 < h < 21$, $0 < k < 21$, $-17 < l < 16$). 4298 unique reflections on the upper half of the reciprocal lattice measured, 3359 with $F > 3\sigma(F)$ used in the analysis.

The structure was solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and refined by block-diagonal least-

* Bis(formato-*O*)bis(urea-*O*)magnesium.

Table 1. Atomic positional and equivalent isotropic thermal parameters for non-H atoms, with e.s.d.'s in parentheses

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq} (Å ²)
Mg1	0.24637 (4)	0.99384 (3)	0.50333 (4)	1.1
Mg2	0.00323 (4)	1.25441 (3)	0.49683 (4)	1.1
O1	0.33739 (8)	0.96467 (7)	0.66157 (9)	1.8
O2	0.13991 (9)	1.01026 (8)	0.34515 (9)	2.0
O3	0.14593 (8)	0.94602 (8)	0.5224 (1)	1.9
O4	0.27517 (8)	0.88325 (7)	0.4611 (1)	1.7
O5	0.22174 (9)	1.10795 (7)	0.5392 (1)	1.9
O6	0.14386 (9)	1.45859 (7)	0.5003 (1)	2.0
O7	0.06013 (9)	1.28359 (7)	0.65394 (9)	2.0
O8	-0.04499 (8)	1.23637 (8)	0.33933 (9)	1.9
O9	0.13272 (8)	1.20488 (7)	0.53851 (9)	1.6
O10	0.04261 (9)	1.36569 (7)	0.4774 (1)	1.9
O11	0.03904 (9)	0.85890 (7)	0.4975 (1)	1.9
O12	0.37326 (8)	0.79684 (7)	0.4600 (1)	1.9
N1	0.4483 (1)	0.9643 (1)	0.8335 (1)	3.8
N2	0.3983 (1)	1.0807 (1)	0.7457 (1)	3.4
N3	0.0519 (1)	1.0287 (1)	0.1706 (1)	3.3
N4	0.2098 (1)	1.0255 (1)	0.2554 (1)	3.2
N5	-0.1257 (1)	1.2297 (1)	0.1641 (1)	3.5
N6	-0.2025 (1)	1.2385 (1)	0.2477 (1)	3.1
N7	0.1561 (1)	1.2861 (1)	0.8296 (1)	3.1
N8	0.1142 (1)	1.1682 (1)	0.7430 (1)	3.0
C1	0.3935 (1)	1.0024 (1)	0.7435 (1)	1.9
C2	0.1350 (1)	1.0223 (1)	0.2610 (1)	1.8
C3	0.1024 (1)	0.8834 (1)	0.4876 (2)	2.1
C4	0.3514 (1)	0.8618 (1)	0.4771 (2)	2.4
C5	-0.1222 (1)	1.2347 (1)	0.2535 (1)	1.8
C6	0.1078 (1)	1.2469 (1)	0.7388 (1)	1.9
C7	0.1499 (1)	1.1345 (1)	0.5291 (1)	2.0
C8	0.1207 (1)	1.3897 (1)	0.5058 (2)	2.2

Table 2. Hydrogen bonds

No.	N—O distance (Å)	Type of bond*
1	N1—H1—O7	Urea-urea
2	N1—H2—O6	Layer-layer
3	N2—H3—O5	Reconnect
4	N2—H4—O10	Layer-layer
5	N3—H5—O2	Urea-urea
6	N3—H6—O11	Layer-layer
7	N4—H7—O3	Layer-layer
	—O1	Urea-urea
8	N4—H8—O6	Reconnect
9	N5—H11—O9	Layer-layer
10	N5—H12—O8	Urea-urea
11	N6—H13—O9	Layer-layer
12	N6—H14—O12	Reconnect
13	†N7—H16—O1	Urea-urea
	—O4	Layer-layer
14	N8—H17—O11	Reconnect
15	N8—H18—O4	Layer-layer

* Urea-urea: (urea)NH—O(urea). Layer-layer: Mg—O(urea)NH—O{formate ion of the next [Mg(HCO₂)₂]_∞ layer}. Reconnect: Mg—O(urea)NH—O{formate ion of the [Mg(HCO₂)₂]_∞ layer containing the initial Mg}.

† N7—H15 is not involved in a hydrogen bond.

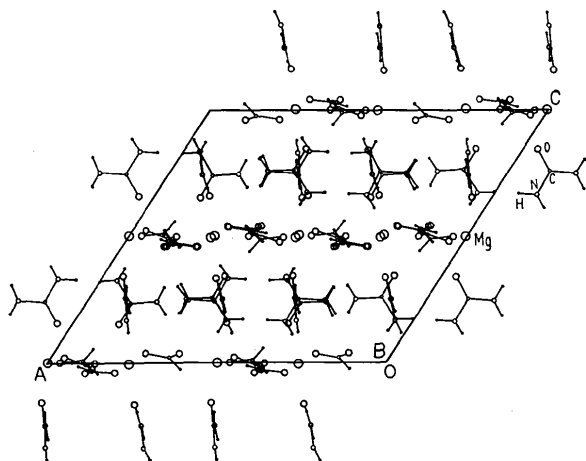


Fig. 1. The *b* projection of the unit cell of Mg(HCO₂)₂·2(NH₂)₂CO.

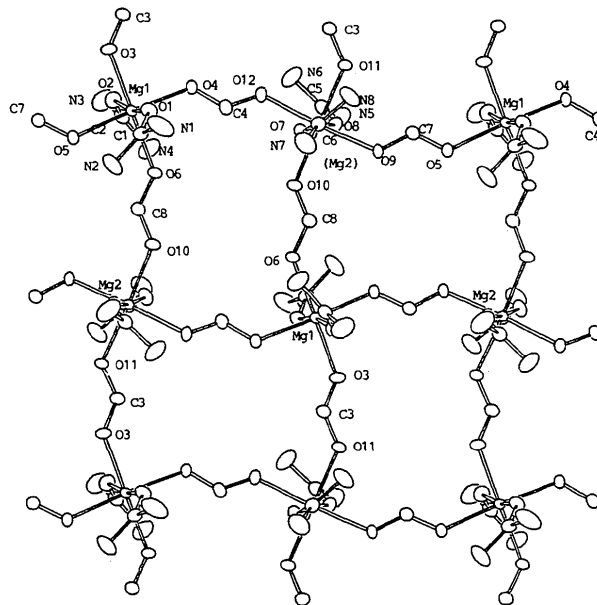


Fig. 2. The *ab* projection of the [Mg(HCO₂)₂]_∞ network in Mg(HCO₂)₂·2(NH₂)₂CO.

squares calculations. H atoms located on a difference electron density map and refined. 351 refined parameters. Anisotropic thermal parameters for Mg, O, N and C, isotropic for H. The function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 1/[\sigma(F)]^2$. An extinction correction was not applied; 8 reflections affected strongly were simply excluded from the refinement. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol IV). wR

for all reflections 0.031, $S = 1.310$, $(\Delta/\sigma)_{\max} 0.09$, $\Delta\rho_{\min}$ and $\Delta\rho_{\max} -0.1248$ and $0.1672 \text{ e } \text{Å}^{-3}$.

The final non-H-atom parameters are given in Table 1.* Computer programs used were those com-

* Lists of final atomic parameters for H atoms, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54771 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0495]

piled and amended by the Kyoto University authors for special use on mini/microcomputers.

Discussion. All interatomic distances and bond angles are normal. For example, Mg—O distances are between 2.055 and 2.114 Å and the deviation of O—Mg—O angles from 90 or 180° is less than 9.32°. The *b* projection of the unit cell is presented in Fig. 1. We can see that the crystal has a double-layer structure: one is the $[\text{Mg}(\text{HCO}_2)_2]_\infty$ network and the other is an assembly of urea molecules. Interlayer bonding is achieved through hydrogen bonds (See Table 2).

A projection of the $[\text{Mg}(\text{HCO}_2)_2]_\infty$ network on the *ab* plane along the *c* direction is shown in Fig. 2. Both magnesium ions are surrounded octahedrally by four square-planar O atoms belonging to different formate ions and by two O atoms of urea molecules. The formate ion bridge between neighboring Mg ions is of the so-called *anti-anti* type seen between *A*-site ions in $\text{Mg}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ (Osaki, Nakai & Watanabe, 1964). The two molecular planes of the

urea coordinated to an Mg^{2+} ion are nearly perpendicular to each other.

It is interesting that the monoclinic Mg lattice can be interpreted as an approximate body-centered tetragonal lattice because $a = b$ and $2c|\cos\beta| = 16.555 \approx a$.

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Acta Cryst. (1992). **C48**, 795–798

Structure of 1,2,3-Tris(dimethylamino)cyclopropenylium Hexachloroniobate(V) and Hexachlorotantalate(V)

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(Received 31 July 1991; accepted 10 October 1991)

Abstract. (1) $[\text{C}_9\text{H}_{18}\text{N}_3][\text{NbCl}_6]$, $M_r = 473.89$, rhombohedral, $R\bar{3}$, $a = 12.7898$ (6), $c = 19.0879$ (9) Å, $V = 2704$ Å³, $Z = 6$, $D_x = 1.746$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.70926$ Å, $\mu = 15.291$ cm⁻¹, $F(000) = 1416$, room temperature, final $R = 0.025$ for F and 862 reflections. (2) $[\text{C}_9\text{H}_{18}\text{N}_3][\text{TaCl}_6]$, $M_r = 561.93$, rhombohedral, $R\bar{3}$, $a = 12.8180$ (3), $c = 19.1170$ (7) Å, $V = 2720$ Å³, $Z = 6$, $D_x = 2.058$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.70926$ Å, $\mu = 68.763$ cm⁻¹, $F(000) = 1608$, room temperature, final $R = 0.023$ for F and 862 reflections. The structures are isomorphic. The crystal structure consists of layers parallel to the *ab* plane; the interaction between anions and cations occurs in the *c* direction thus forming columns distributed in rhombohedral sequence.

Introduction. The structure of the tris(dimethylamino)cyclopropenylium ion has been reported by Ku & Sundaralingam (1972). Our structure determination is part of investigations on the salts of the tris(dimethylamino)cyclopropenylium ion and inorganic complex anions (Yoshida & Tawara, 1971; Weiss & Schlöter, 1975). In several cases these salts show – as do the title compounds – interesting outer-sphere charge-transfer interactions between cation and anion leading to intensely coloured solids although the ionic components of the salts are colourless (Weiss, 1979).

Experimental. In an N₂ atmosphere 576 mg NbCl₅ was dissolved in a mixture of 20 ml dry CH₃CN and 0.5 ml SOCl₂. A solution of 434 mg tris(dimethyl-