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Structures of Hydrothermally Synthesized Cobalt(II) Carbonate and Nickel(II) Carbonate

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Abstract. CoCO_3 , $M_r = 118.94$, rhombohedral, $R\bar{3}c$, $a = 4.6618(5)$, $c = 14.963(2)$ Å, $V = 281.62$ Å³, $Z = 6$, $D_x = 4.208$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.710688$ Å, $\mu = 8.5$ mm⁻¹, $F(000) = 342$, room temperature, $R = 0.040$ for 287 observed reflections up to $\sin \theta/\lambda = 1.076$ Å⁻¹. NiCO_3 , $M_r = 118.72$, rhombohedral, $R\bar{3}c$, $a = 4.6117(5)$, $c = 14.735(2)$ Å, $V = 271.39$ Å³, $Z = 6$, $D_x = 4.358$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.710688$ Å, $\mu = 10.0$ mm⁻¹, $F(000) = 348$, room temperature, $R = 0.057$ for 235 observed reflections up to $\sin \theta/\lambda = 1.076$ Å⁻¹. Within the calcite-type carbonate structures the variability of the C–O bond lengths as well as the correlation of the M–O distances and the distortion of the MO_6 octahedra with the shortest interpolyhedral O–O contacts are discussed. Both compounds NiCO_3 and CoCO_3 were synthesized under hydrothermal conditions.

Introduction. The crystal structures of magnesite, calcite, rhodochrosite, siderite, and smithsonite were recently refined by standard single-crystal X-ray methods (Effenberger, Mèreiter & Zemmann, 1981). To complete this series, comparable refinements of CoCO_3 and NiCO_3 were performed, because these structure

determinations were based on X-ray powder data only (cf. Graf, 1961, 1969). Within the series of trigonal carbonates the Ni atom has the smallest atomic radius, and for CoCO_3 the smallest ratio (longer O–O edge)/(shorter O–O edge) within the MO_6 octahedra was calculated from a theoretical structure model (Effenberger *et al.*, 1981). Therefore, it was expected that detailed crystal-structure refinements of both compounds could contribute to some aspects of stereochemistry in the series under consideration. Single crystals of CoCO_3 and NiCO_3 were grown under hydrothermal conditions (Reiterer, 1980; Gamsjäger, Reiterer & Heindl, 1982).

Experimental. Both compounds: synthetic crystals, rhombohedra, Stoe AED-2 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, $2\theta/\omega$ scan, step number increased for (α_1, α_2) splitting, step width 0.03°, step time 0.5 to 1.5 s per step, data collection up to $2\theta = 100^\circ$; three standard reflections with no significant intensity variation.

CoCO_3 : 0.08 × 0.08 × 0.08 mm, lattice parameters from 73 reflections up to $2\theta = 40^\circ$; four ψ scans for absorption correction (transmission factors from 0.52

to 0.61); merging of 1190 reflections (min. 60 steps per reflection, $h:0-10$, $k:0-10$, $l:-30-30$) yielded 328 unique data of which 287 with $F_o > 3\sigma(F_o)$ used for refinement [$R(I)_{\text{int}} = 0.039$]. $R = 0.040$ and $wR = 0.037$, $w = 1/|\sigma(F_o)|^2$; max. $\Delta/\sigma < 10^{-3}$; max. and min. height in final difference Fourier map 1.81 and $-1.31 \text{ e } \text{Å}^{-3}$. The value g for the isotropic secondary extinction (Zachariasen, 1967) is $9.1 (74) \times 10^{-6}$.

NiCO_3 : $0.04 \times 0.04 \times 0.04 \text{ mm}$, lattice parameters from 14 reflections up to $2\theta = 25^\circ$; three ψ scans for absorption correction (transmission factors from 0.66 to 0.74); merging of 776 measured reflections (min. 60 steps per reflection, $h:0-8$, $k:0-8$, $l:-27-27$) yielded 318 unique data of which 235 with $F_o > 3\sigma(F_o)$ used for refinement [$R(I)_{\text{int}} = 0.045$]. $R = 0.057$ and $wR = 0.042$, $w = 1/|\sigma(F_o)|^2$; max. $\Delta/\sigma < 10^{-3}$; max. and min. height in final difference Fourier map 1.9 and $-1.5 \text{ e } \text{Å}^{-3}$. The value g for the isotropic secondary extinction (Zachariasen, 1967) is $1.8 (13) \times 10^{-5}$.

The values given for the lattice parameters agree well with those values compiled by Graf (1961, 1969, with references). Correction for Lorentz and polarization effects; atomic scattering factors and anomalous-dispersion factors for neutral atoms (*International Tables for X-ray Crystallography*, 1974). All calculations performed with program system *STRUCSY* (Fa. Stoe & Cie, Darmstadt, Federal Republic of Germany). The structural parameters for calcite (Effenberger *et al.*, 1981) were used as starting parameters. Several cycles of full-matrix least-squares refinement on F with anisotropic temperature parameters gave the structure parameters listed in Table 1.* Some important interatomic distances are summarized in Table 2.

Discussion. As pointed out by Effenberger *et al.* (1981) for the calcite-type carbonates $M\text{CO}_3$ with $M = \text{Mg}$, Ca , Mn , Fe , and Zn and as extended by the recent work for CoCO_3 and NiCO_3 the variation of the C—O bond lengths is very slight, if at all real. So in all the calcite-type carbonate structures the C—O distances are in the range from 1.2852 (4) Å (magnesite) to 1.291 (2) Å (NiCO_3). Only for calcite, the carbonate with the largest atomic radius of the M atom, the C—O bond length at 1.2815 (6) Å is considerably shorter than the comparable values in the other calcite-type carbonates. As considered by the previous authors, this value might be simulated by a larger thermal motion observed for all the atoms within this structure. The relatively large standard deviation for the atomic coordinates in NiCO_3 and in some respect also in CoCO_3 , result from the small size of the crystals used for the recent data collection.

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42497 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic fractional coordinates and anisotropic temperature parameters (Å^2) with *e.s.d.'s* in parentheses

Space group $R\bar{3}c$ (D_{3d}^6) (No. 167). The anisotropic temperature factor is of the form $\exp[-2\pi^2(\sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j)]$.

		CoCO_3	NiCO_3
6 M on 6(b) (000), etc.	U_{11}	0.0057 (2)	0.0068 (2)
	U_{33}	0.0069 (2)	0.0058 (3)
	U_{11}	0.0057 (7)	0.0074 (11)
6 C on 6(a) (00 $\frac{1}{2}$), etc.	U_{33}	0.0059 (9)	0.0039 (14)
	\bar{x}	0.7234 (4)	0.7201 (6)
18 O on 18(e) ($\bar{x}\bar{x}\frac{1}{2}$), etc.	U_{11}	0.0064 (5)	0.0053 (6)
	U_{33}	0.0094 (5)	0.0084 (9)
	U_{12}	0.0021 (6)	0.0016 (8)
	U_{13}	-0.0010 (3)	-0.0008 (4)

Table 2. Interatomic distances (Å) with *e.s.d.'s* in parentheses

		CoCO_3	NiCO_3
M—O	6 ×	2.110 (1)	2.076 (2)
O—O	3 × ^a	2.947 (4)	2.905 (5)
O—O	3 × ^b	3.019 (2)	2.972 (3)
C—O	3 ×	1.290 (1)	1.291 (2)
O—O	3 ×	2.233 (3)	2.235 (5)

(a) Edge of the MO_6 polyhedron parallel to (00.1). (b) Edge of the MO_6 polyhedron inclined to (00.1).

The MO_6 octahedra are in all calcite-type structures somewhat elongated parallel to [001]. The ratio of longer edge to shorter edge is 1.024 for CoCO_3 and 1.023 for NiCO_3 . For the other $M\text{CO}_3$ compounds this ratio varies from 1.0283 (smithsonite) to 1.0455 (calcite). This ratio together with the value for the M—O distances causes a variation of a short interpolyhedral O—O contact, which is no edge of any coordination figure (Effenberger *et al.*, 1981). This distance measures 2.807 (2) Å in NiCO_3 and 2.844 (1) Å in CoCO_3 . The comparable values in the other calcite-type carbonates vary from 2.8485 (5) Å in magnesite to 3.1883 (5) Å in calcite.

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