

## Structures of Mercury(I) Nitrite and Lithium Disilver Trinitrite

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**Abstract.**  $\text{Hg}_2(\text{NO}_2)_2$  (I),  $M_r = 493.2$ , monoclinic,  $P2_1/c$ ,  $a = 4.435$  (1),  $b = 10.344$  (2),  $c = 6.301$  (2) Å,  $\beta = 108.74$  (2)°,  $V = 273.7$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 5.99$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 55.96$  mm<sup>-1</sup>,  $F(000) = 393.4$ ,  $T = 297$  (1) K, final  $R = 0.048$  for 623 observed unique reflections.  $\text{Ag}_2\text{Li}(\text{NO}_2)_3$  (II),  $M_r = 360.7$ , monoclinic,  $C2/c$ ,  $a = 10.166$  (1),  $b = 7.575$  (2),  $c = 8.479$  (1) Å,  $\beta = 91.27$  (1)°,  $V = 652.8$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.67$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 5.94$  mm<sup>-1</sup>,  $F(000) = 664.7$ ,  $T = 297$  (1) K, final  $R = 0.033$  for 902 observed unique reflections. In (I) there exists a nearly planar centrosymmetric unit of  $\text{N} \begin{array}{c} \diagup \text{O} \cdots \text{Hg} \cdots \text{O} \\ \diagdown \text{O} \cdots \text{Hg} \cdots \text{O} \end{array} \text{N}$  with Hg-Hg distance 2.520 (2) Å and Hg...O distances 2.244 (11) and 2.577 (11) Å. In (II) nearly coplanar units of  $\text{Ag} \cdots \text{N} \begin{array}{c} \diagup \text{O} \cdots \text{Ag} \\ \diagdown \text{O} \cdots \text{Ag} \end{array}$  with a short Ag...N distance of 2.241 (8) Å on average were recognized, suggesting some Ag...N covalency. The  $\text{Li}^+$  lies on a center of symmetry and constitutes a link in a linear chain with one of the two independent nitrite ions, which is disordered between two equivalent positions. Geometric distortion of  $\text{NO}_2^-$  induced by an asymmetric  $\text{Ag}^+ \cdots \text{O}$  or  $\text{Hg}_2^{2+} \cdots \text{O}$  short contact is recognized.

**Introduction.** The perturbation of  $\text{NO}_2^-$  by a post-transition-metal cation causes a yellow color (McGlynn, Azumi & Kumar, 1981; Yamashita & Azumi, 1984) and the structure of  $\text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$  suggested that the metal cation on the bridge position between two O atoms of a nitrite ion,  $\text{Pb}^{2+} \cdots \begin{array}{c} \text{O} \\ \diagup \cdots \text{N} \\ \diagdown \cdots \text{O} \end{array}$ , plays an important role (Ohba, Nosé & Saito, 1985).

On the other hand, there exist not only  $\text{Ag}^+ \cdots \begin{array}{c} \text{O} \\ \diagup \cdots \text{N} \\ \diagdown \cdots \text{O} \end{array}$  but also  $\text{Ag}^+ \cdots \text{N} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$  interactions in  $\text{AgNO}_2$  (Ohba & Saito, 1981). Structures of the yellow title crystals were determined to study further the interaction between  $\text{NO}_2^-$  and the post-transition-metal cations,  $\text{Hg}_2^{2+}$  or  $\text{Ag}^+$ .

**Experimental.** (I): Yellow prisms grown overnight from mercury in 16 wt% nitric acid at 306 K (Rây, 1905). A

small spherical specimen was prepared to minimize absorption. The crystal easily pulverized by grinding or cutting. A spherical crystal ground with sandpaper was etched successfully from ca 0.4 to 0.213 (13) mm in diameter by mother liquor. Rigaku AFC-5 four-circle diffractometer, graphite monochromator. Laue group  $2/m$ , systematic absences  $h0l$  with  $l$  odd and  $0k0$  with  $k$  odd; cell parameters refined by least squares for 19  $2\theta$  values ( $20 < 2\theta < 30^\circ$ ), intensity measurement performed up to  $2\theta = 60^\circ$  ( $h -6 \rightarrow 6$ ,  $k -14 \rightarrow 14$ ,  $l -8 \rightarrow 8$ ),  $\omega$ -scan width  $1.9^\circ$ , scan speed  $4^\circ \text{ min}^{-1}$ . Variation of  $|F_o|$  of five standard reflections,  $0.98 \leq \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.00$ . 3089 reflections measured, 2093 observed reflections with  $|F_o| > 3\sigma(|F_o|)$ , 623 unique ( $R_{\text{int}} = 0.04$ ). Variation of  $|F(020)|$  and  $|F(060)|$  with  $\psi$  scan 4.5 and 3.6%. This corresponds to the variation of  $|F_o|$  arising from crystal non-sphericity, 3-9% (Flack & Vincent, 1978). Correction for absorption ( $\mu_r = 5.95$ ,  $0.0040 \leq A \leq 0.0178$ ). Structure solved by Patterson and Fourier methods. Coordinates and anisotropic thermal parameters refined,  $\sum w||F_o| - |F_c||^2$  minimized,  $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ , final  $R = 0.048$ ,  $wR = 0.047$ ,  $S = 1.93$  for 623 unique reflections.\* No secondary-extinction effect. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Reflection/parameter ratio 16.8,  $\Delta/\sigma < 0.27$ , max. and min. heights in final difference synthesis 1.8 and  $-3.5 \text{ e } \text{Å}^{-3}$  except for a peak of  $4.6 \text{ e } \text{Å}^{-3}$  at  $0.7 \text{ Å}$  from Hg. UNICSIII program system (Sakurai & Kobayashi, 1979), FACOM M-380R computer of this university.

(II): Yellow plate-like crystals grown from  $\text{LiNO}_2$  aqueous solution saturated with  $\text{AgNO}_2$ . Spherical crystal of diameter 0.42 (3) mm ground with sandpaper, slightly hygroscopic. Laue group  $2/m$ , systematic absences  $hkl$  with  $h + k$  odd and  $h0l$  with  $h$  odd or  $l$  odd; cell parameters refined by least squares for 20  $2\theta$  values ( $20 < 2\theta < 30^\circ$ ), intensity measurement performed to  $2\theta = 60^\circ$  ( $h -14 \rightarrow 14$ ,  $k 0 \rightarrow 10$ ,  $l -11 \rightarrow 11$ ),  $\theta$ - $2\theta$  scan, scan speed  $6^\circ \text{ min}^{-1}$  in  $\theta$ .

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42501 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Variation of  $|F_o|$  of five standard reflections,  $0.96 \leq |F_o|/|F_o|_{\text{initial}} \leq 1.01$ , 1893 reflections measured, 1767 observed reflections with  $|F_o| > 3\sigma(|F_o|)$ , 902 unique ( $R_{\text{int}} = 0.011$ ). Absorption correction ( $\mu r = 1.25$ ,  $0.176 \leq A \leq 0.200$ ). Structure solved by heavy-atom method. Coordinates and anisotropic thermal parameters refined with full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979),  $\sum w||F_o| - |F_c||^2$  minimized,  $w^{-1} = \sigma^2(|F_o|) + (0.02|F_o|)^2$ , reduction of  $R$  from 0.059 to 0.033 by introducing an isotropic secondary-extinction-correction parameter (Zachariasen, 1967),  $g = 0.42(4) \times 10^{-4}$ ,  $wR = 0.067$ ,  $S = 3.03$  for 902 unique reflections.\* Smallest extinction-correction factor ( $F_o^2/F_c^2$ ) 0.36 for 111. Reflection/parameter ratio 12.7,  $\Delta/\sigma \leq 0.003$ , max. and min. heights in final difference synthesis 1.64 and  $-0.92 \text{ e } \text{Å}^{-3}$ .

**Discussion.** We were informed by the Co-editor that the structure of (I) had just been published by English, Röhms & Schutte (1985), here referred to as ERS. ERS and this study have quite independently derived essentially the same structure. A lower  $R$  factor, 0.048 for 623 unique reflections (0.067 for 375 reflections in ERS), and smaller e.s.d.'s in the atomic parameters than those of ERS were achieved by preparing a small spherical specimen *ca* 0.2 mm in diameter. ERS used a prismatic crystal,  $0.4 \times 0.4 \times 0.4 \text{ mm}$ , and applied an empirical absorption correction. Our atomic coordinates ( $x, y, z$ ) are related to those of ERS ( $x', y', z'$ ) by the equation,  $y' = -y$ . The largest difference is  $4.6\sigma$  for  $x$  of O(2).

Final atomic coordinates and interatomic distances and angles are presented in Tables 1 and 2. The crystal structure of (I) is shown in Fig. 1(a). The  $\text{Hg}_2^{2+}$  ion lies on the center of symmetry. A nearly planar unit of  $\text{NO}_2 \cdots \text{Hg}_2^{2+} \cdots \text{O}_2\text{N}^-$  is stacked with its normal inclined by  $61.3^\circ$  to **b**. The shortest interatomic distance between the planar units is  $2.826(13) \text{ Å}$  for  $\text{Hg} \cdots \text{O}(1^i)$ . Around the nitrite ion, there is no other neighboring  $\text{Hg}_2^{2+}$  ion less than  $0.5 \text{ Å}$  from the  $\text{NO}_2$  plane. Thus, it is revealed that the yellow color of  $\text{Hg}_2(\text{NO}_2)_2$  is induced by the  $\text{Hg}_2^{2+}$  cation on the bridge position of the nitrite O atoms. As seen from Fig. 1(b), the angle  $\text{Hg} \cdots \text{O}(1) \cdots \text{N}$  is  $173.3(3)^\circ$  owing to the *sp* configuration of the Hg atoms (Wells, 1984). The  $\text{Hg} \cdots \text{O}(1) \cdots \text{N}$  angle of  $105.8(9)^\circ$  corresponds well to the direction of a lone pair on the nitrite O atom, *ca*  $110^\circ$  (Ohba, Kikkawa & Saito, 1985). However, the  $\text{Hg} \cdots \text{O}$  bond does not seem to be strong because the bond length is longer by  $0.11(1) \text{ Å}$  than that of the complex aqua-cation  $(\text{H}_2\text{O} \cdots \text{Hg} \cdots \text{OH}_2)^{2+}$  in  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$   $2.13(2) \text{ Å}$  (Grdenić, Sikirica & Vikić, 1975).

$\text{NO}_2(2)$  of (II) is disordered over a pair of symmetry-related sites connected with the center of symmetry at  $(\frac{1}{2}, 0, \frac{1}{2})$  (see Fig. 2). This can be interpreted as orientational disorder as observed in  $\text{NaNO}_2$  (Kay & Frazer, 1961), where the probability for each of the

orientations  $\text{Ag} \cdots \text{O} \cdots \text{N} \cdots \text{O} \cdots \text{Ag}$  and  $\text{Ag} \cdots \text{N} \cdots \text{O} \cdots \text{O} \cdots \text{Ag}$  is  $\frac{1}{2}$ .

The  $\text{Li}^+$  is surrounded octahedrally by six nitrite O atoms with distances ranging from  $2.118(4)$  to  $2.165(8) \text{ Å}$ . The  $\text{Li}^+$  and disordered  $\text{NO}_2(2)$  ions form linear chains running nearly along  $[110]$  at  $z \approx 0$  and

Table 1. *Positional parameters* ( $\times 10^4$ ; for Ag  $\times 10^5$ ) and *equivalent isotropic temperature factors* (Hamilton, 1959)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{Å}^2 \times 10)$
Compound (I)				
Hg	1531 (2)	808 (1)	1441 (1)	31
N	6559 (34)	2045 (15)	4855 (25)	35
O(1)	3716 (26)	2366 (13)	3932 (19)	36
O(2)	7254 (28)	1012 (12)	4184 (24)	39
Compound (II)				
Ag	38397 (4)	28952 (5)	6251 (4)	30
Li	2500	2500	5000	25
N(1)	1600 (4)	7 (5)	2465 (4)	21
N(2)*	5175 (7)	459 (10)	4918 (10)	22
O(11)	1417 (3)	-431 (5)	1039 (4)	27
O(12)	1830 (4)	1586 (5)	2715 (4)	28
O(21)*	3963 (7)	423 (12)	5041 (10)	27
O(22)*	5697 (9)	-1071 (11)	5163 (14)	37

\* 50% site-occupation factor.

Table 2. *Interatomic distances* (Å) and *angles* ( $^\circ$ )

Compound (I)			
N—O(1)	1.253 (17)	Hg—O(1 <sup>i</sup> )	2.826 (13)
N—O(2)	1.221 (17)	Hg—N	2.852 (13)
O(1)—N—O(2)	113.8 (13)	Hg—O(2 <sup>ii</sup> )	2.955 (15)
		Hg—N <sup>iii</sup>	3.066 (11)
Hg—O(1)	2.244 (11)		
Hg—O(2)	2.577 (11)	Hg—Hg <sup>iv</sup>	2.520 (2)
Symmetry code: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii) $x - 1, y, z$ ; (iii) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iv) $-x, -y, -z$ .			
Compound (II)			
N(1)—O(11)	1.264 (5)	Ag—O(11 <sup>v</sup> )	2.925 (3)
N(1)—O(12)	1.236 (5)	Ag—O(12 <sup>vi</sup> )	2.925 (3)
O(11)—N(1)—O(12)	116.2 (4)	Ag—N(2 <sup>vii</sup> )	2.949 (8)
		Ag—O(21 <sup>viii</sup> )	2.979 (8)
N(2)—O(21)	1.239 (10)		
N(2)—O(22)	1.290 (11)	Li—O(11 <sup>ix</sup> )	2.118 (4)
O(21)—N(2)—O(22)	111.9 (8)	Li—O(11 <sup>x</sup> )	2.118 (4)
		Li—O(22 <sup>xi</sup> )	2.136 (9)
Ag—N(2 <sup>i</sup> )	2.154 (8)	Li—O(22 <sup>xii</sup> )	2.136 (9)
Ag—N(1 <sup>ii</sup> )	2.327 (4)	Li—O(12)	2.154 (3)
Ag—O(22 <sup>iii</sup> )	2.379 (9)	Li—O(12 <sup>iv</sup> )	2.154 (3)
Ag—O(11 <sup>v</sup> )	2.394 (4)	Li—O(21)	2.165 (8)
Ag—O(21 <sup>vi</sup> )	2.565 (9)	Li—O(21 <sup>v</sup> )	2.165 (8)
Ag—O(12)	2.908 (4)		
Symmetry code: (i) $1-x, y, \frac{1}{2}-z$ ; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (iii) $x, -y, -\frac{1}{2}+z$ ; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, -z$ ; (v) $\frac{1}{2}+x, \frac{1}{2}+y, z$ ; (vi) $x, -y, \frac{1}{2}+z$ ; (vii) $-\frac{1}{2}+x, \frac{1}{2}+y, z$ ; (viii) $1-x, -y, 1-z$ ; (ix) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$ ; (x) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ .			

\* See deposition footnote.

nearly along  $[1\bar{1}0]$  at  $z \approx \frac{1}{2}$  as shown in Fig. 3. The  $\text{NO}_2^-(1)$  ion links two  $\text{Li}^+$  in the chains running along different directions. The  $\text{Ag}^+$  ion lies near the center of three nitrite ions.

The yellow color of these crystals is a complement of the absorption band around 450 nm corresponding to the  $T_1 \leftarrow S_0$  spin-forbidden transition of the  $\text{NO}_2^-$  ion, which is enhanced by spin-orbit coupling through the covalency between the  $\text{NO}_2^-$  and the post-transition-metal cation (McGlynn *et al.*, 1981). Fig. 4 shows the arrangement of  $\text{Ag}^+$  and  $\text{Li}^+$  around the nitrite ions, with the shifts from the  $\text{NO}_2$  plane less than 0.5 Å. Close contact between  $\text{Ag}^+$  and N was observed. The mean  $\text{Ag} \cdots \text{N}$  interatomic distance is 2.241 (8) Å, which is shorter by 0.063 (8) Å than that in  $\text{AgNO}_2$  (Ohba & Saito, 1981). The short contacts of the metal cations to the nitrite O atoms are observed in (I), (II) and  $\text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$  (Ohba, Nosé & Saito, 1985). The  $\text{Ag} \cdots \text{N}$  covalency may be exceptional. The geometric distortion of  $\text{NO}_2^-$  induced by an asymmetric short contact is recognized. The shorter the  $\text{Hg} \cdots \text{O}$  or  $\text{Ag} \cdots \text{O}$  distance is, the longer becomes the N—O bond length, in correspondence with observations in transition-metal nitrite complexes, for example  $[\text{Cu}(2,2'\text{-bipyridyl})_2(\text{O}_2\text{N})]\text{NO}_3$  (Procter & Stephens, 1969) and  $[\text{Ni}(2,2'\text{-bipyridyl})_2(\text{O}_2\text{N})]\text{NO}_3$  (Finney, Hitchman, Kepert, Raston, Rowbottom & White, 1981), and in  $\text{AgC}(\text{CN})_2\text{NO}_2$  (Chow & Britton, 1974). The bond angle  $121.3(3)^\circ$  for  $\text{N}(1)\text{—O}(12) \cdots \text{Li}^{\text{ix}}$  suggests  $sp^2$  hybridization of the nitrite O atom.

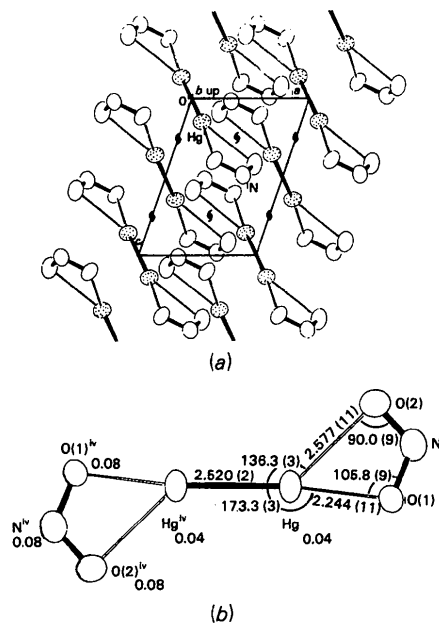


Fig. 1. (a) Projection of the structure of (I) along  $b$  and (b) the  $\text{NO}_2 \cdots \text{Hg}_2 \cdots \text{O}_2\text{N}$  unit. Atoms are also labeled with their deviations (Å) from the plane of one  $\text{NO}_2^-$ . Distances in Å, angles in  $^\circ$ .

However, the  $\text{N—O} \cdots \text{Li}$  angles of  $\text{NO}_2^-(2)$  are not close to  $120^\circ$ , suggesting that it is in a less stable position, consistent with the observed disorder.

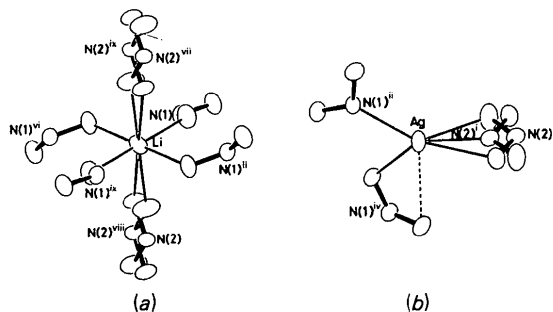


Fig. 2. Environment of (a)  $\text{Li}^+$  and (b)  $\text{Ag}^+$  ions. The symmetry code is given in Table 2.

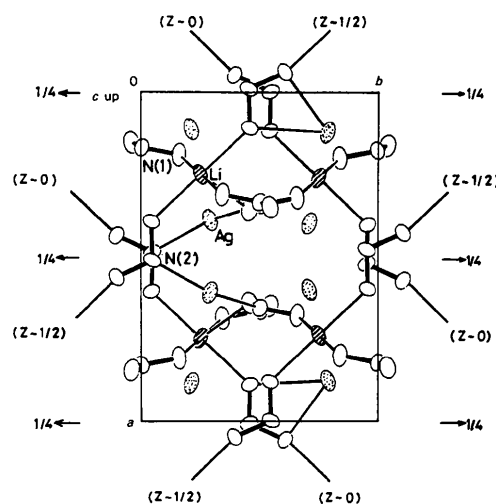


Fig. 3. A view of the structure of (II) perpendicular to  $ab$ . Only one of the two possible orientations for  $\text{NO}_2^-(2)$  is drawn for simplicity. Hatched and dotted ellipsoids represent  $\text{Li}^+$  and  $\text{Ag}^+$  ions respectively.

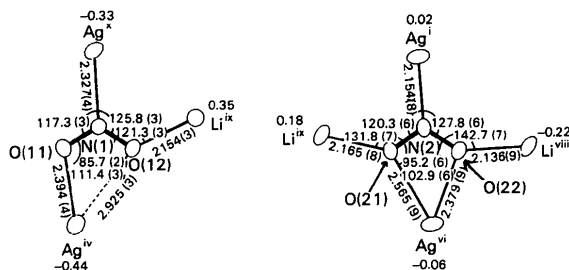


Fig. 4. Arrangement of metal cations around the  $\text{NO}_2^-$  ions in (II) with distances from the  $\text{NO}_2$  plane less than 0.5 Å, which are indicated by numbers near the atom labels. The symmetry code is given in Table 2. Distances in Å, angles in  $^\circ$ .

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

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**Abstract.**  $\text{CoCO}_3$ ,  $M_r = 118.94$ , rhombohedral,  $R\bar{3}c$ ,  $a = 4.6618$  (5),  $c = 14.963$  (2) Å,  $V = 281.62$  Å<sup>3</sup>,  $Z = 6$ ,  $D_x = 4.208$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.710688$  Å,  $\mu = 8.5$  mm<sup>-1</sup>,  $F(000) = 342$ , room temperature,  $R = 0.040$  for 287 observed reflections up to  $\sin \theta/\lambda = 1.076$  Å<sup>-1</sup>.  $\text{NiCO}_3$ ,  $M_r = 118.72$ , rhombohedral,  $R\bar{3}c$ ,  $a = 4.6117$  (5),  $c = 14.735$  (2) Å,  $V = 271.39$  Å<sup>3</sup>,  $Z = 6$ ,  $D_x = 4.358$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.710688$  Å,  $\mu = 10.0$  mm<sup>-1</sup>,  $F(000) = 348$ , room temperature,  $R = 0.057$  for 235 observed reflections up to  $\sin \theta/\lambda = 1.076$  Å<sup>-1</sup>. 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  $\text{MO}_6$  octahedra with the shortest interpolyhedral O–O contacts are discussed. Both compounds  $\text{NiCO}_3$  and  $\text{CoCO}_3$  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 & Zemann, 1981). To complete this series, comparable refinements of  $\text{CoCO}_3$  and  $\text{NiCO}_3$  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  $\text{CoCO}_3$  the smallest ratio (longer O–O edge)/(shorter O–O edge) within the  $\text{MO}_6$  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  $\text{CoCO}_3$  and  $\text{NiCO}_3$  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  $(\alpha_1, \alpha_2)$  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.

$\text{CoCO}_3$ : 0.08 × 0.08 × 0.08 mm, lattice parameters from 73 reflections up to  $2\theta = 40^\circ$ ; four  $\psi$  scans for absorption correction (transmission factors from 0.52