Inorganica Chimica Acta, 41 (1980) 185–194
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Synthesis and Crystal Structures of Lithium and of Sodium Bis(dithioxalato)-nickelate(II). Comparison with the Potassium Derivatives

F. MAURY and A. GLEIZES*

Laboratoire de Chimie de Coordination du C.N.R.S. associé à l'Université Paul Sabatier de Toulouse, 205 rte de Narbonne, 31400 Toulouse, France

Received January 2, 1980

Lithium and sodium bis(dithioxalato)nickelate(II) dihydrates, $Li_2Ni(S_2C_2O_2)_2\cdot 2H_2O$ *and* $Na_2Ni(S_2C_2O_2)_2\cdot 2H_2O$, *have been synthesized from potassium bis(dithioxalato)nickelate(II)* $K_2Ni(S_2C_2O_2)_2$. *Both these compounds crystallize in the triclinic system, space group* $P\bar{1}$, *with Z = 1 formula unit per cell, the parameters being:* a = *7.516(3)* Å, b = *10.644(5)* Å, c = *3.666(1)* Å, α = *95.47(3)°*, β = *87.62(4)° and* γ = *108.73(3)° for the lithium compound;* a = *7.680(2)* Å, b = *11.050(4)* Å, c = *3.785(1)* Å, α = *90.69(3)°*, β = *93.77(2)° and* γ = *110.33(2)° for the sodium compound. The crystal structures were determined by X-ray single-crystal techniques. Full-matrix least-squares refinement of 80 variables gave final values of the conventional* R *index (on F) of 0.027 for the 1712 observations above background in the case of the lithium compound and of 0.035 for the 1355 observations above background in the case of the sodium compound. Like in black* $K_2Ni(S_2C_2O_2)_2$ *previously studied, the structures contain planar anions* $Ni(S_2C_2O_2)_2^{2-}$ *stacked along the short cell axis, with normals to molecular planes not colinear with the stacking axis. The influence of the cation on the characteristics of the stacks is discussed. The presence of water molecule relates these compounds to the homologous sodium bis(oxalato)cuprate(II) dihydrate,* $Na_2Cu(C_2O_4)_2\cdot 2H_2O$ *[1].*

Introduction

In a previous paper [2] we have described the synthesis and the crystal structure of a new form of potassium bis(dithioxalato)nickelate(II): this compound, which had long been known solely as a red iridescent crystalline material [3], may also be obtained as black glittening crystals. Unlike that of the red form, the crystal structure of the black form is of the one-dimensional type, being made of stacked anions $Ni(S_2C_2O_2)_2^{2-}$ and of chains of cations K^+. Both anionic stacks and cationic chains run parallel to the twofold axis of the monoclinic cell. The anions $Ni(S_2C_2O_2)_2^{2-}$ are quasi-planar; they are tilted by 124° on the stacking axis. Intrastack Ni–Ni spacings amount to 4.191 Å, which rules out the possibility of strong intrastack interactions. This distance is also the closest possible approach between potassium atoms in a cationic chain and is then crystallographically imposed. It could be possibly shortened in two ways: either on partially oxidizing $K_2Ni(S_2C_2O_2)_2$, as was done for instance with $K_2Pt(C_2O_4)_2\cdot xH_2O$ [4], or on decreasing the size or increasing the charge of the cationic species. As the former way has failed so far [2], we are investigating the latter.

We report here on the synthesis and crystal structures of both the lithium and the sodium bis(dithioxalato)nickelate(II). Their structures will be discussed in terms of comparison with those of black and red $K_2Ni(S_2C_2O_2)_2$.

Experimental

Synthesis and Crystal Studies

Lithium and sodium bis(dithioxalato)nickelates(II) were obtained by mixing potassium bis(dithioxalato)nickelate(II), $K_2Ni(S_2C_2O_2)_2$, prepared as described in [3], with lithium or sodium perchlorate in concentrated aqueous solution. Potassium perchlorate precipitates and is eliminated by filtration. On evaporation of the solution, black glittening crystals separate.

The density was measured by flottation in a mixture of methyl iodide and carbon tetrachloride and was found equal to 2.07 ± 0.02 g/cm^3 for the lithium compound and 2.05 ± 0.02 g/cm^3 for the sodium compound. X-ray photographs of both types of crystal were taken using a Stoe precession camera with MoK_α radiation: for both compounds a triclinic cell has been found with approximate parameters: a = 7.51 Å, b = 10.6 Å, c = 3.7 Å, α = 95°, β = 88° and γ = 108° for the lithium salt, and a = 7.68 Å, b = 11.0 Å, c = 3.79 Å, α = 91°, β = 94° and γ = 110°

---

*Author to whom all correspondence should be addressed.

TABLE I. Experimental Crystallographic Data for $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$.

1) Physical and Crystallographic Data:

Crystal system: triclinic

Space group: $P\bar{1}$

a = 7.516(3) Å
b = 10.644(5) Å
c = 3.666(1) Å
α = 95.47(3)°
β = 87.62(4)°
γ = 108.73(3)°

Molecular weight: 348.92

ρ_{meas} = 2.07(2) g cm^3
ρ_X = 2.09 g cm^3
V = 276.5 Å^3
Z = 1

Morphology: Flat parallelepiped
(0.016 × 0.012 × 0.004) cm
Faces of forms $\{110\}$ $\{\bar{1}10\}$ $\{0\bar{2}1\}$

Absorption factor: μ_{MoK_α} = 24.91 cm^{-1}

Transmission factors $\begin{cases} \text{minimum} = 0.594 \\ \text{maximum} = 0.906 \end{cases}$

2) Data Collection:

Temperature: 294 K; Radiation: $\lambda(MoK_\alpha)$ = 0.71069 Å
Monochromatization: oriented graphite crystal
Crystal-detector distance : 207 mm
Detector window: height = 4 mm; width = 4 mm
Take-off angle: 3.5°
Scan mode: θ–2θ
Maximum Bragg angle: 35°
Scan angle: $\Delta\theta = \Delta\theta_0 + B \tan\theta$; $\Delta\theta_0$ = 1.10°; B = 0.347
Values determining the scan speed:
SIGPRE = 0.33 SIGMA = 0.018
VPRE = 10°/mn TMAX = 40 s
Standard intensity reflexions: 040, 300, $2\bar{3}1$ measured every 3600 s
Independent recorded reflexions: 2419
Utilized reflexions: 1712 ($F_0^2 > 3\sigma(F_0^2)$)

TABLE II. Experimental Crystallographic Data for $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$.

1) Physical and Crystallographic Data:

Crystal system: triclinic

Space group: $P\bar{1}$

a = 7.680(2) Å
b = 11.050(4) Å
c = 3.785(1) Å
α = 90.69(3)°
β = 93.77(2)°
γ = 110.33(2)°

Molecular weight: 381.02

ρ_{meas} = 2.05(2) g cm^{-3}
ρ_X = 2.11 g cm^{-3}
V = 300.4 Å^3
Z = 1

Morphology: Flat parallelepiped
(0.016 × 0.009 × 0.005) cm
Faces of forms $\{100\}$ $\{1\bar{1}0\}$ $\{001\}$

Absorption factor: μMoK_α = 23.66 cm^{-1}

Transmission factors $\begin{cases} \text{minimum} = 0.819 \\ \text{maximum} = 0.941 \end{cases}$

2) Data Collection:

Temperature: 293 K; Radiation: $\lambda(MoK_\alpha)$ = 0.71069 Å
Monochromatization: oriented graphite crystal
Crystal-detector distance: 207 mm
Detector window: height = 4 mm; width = 4 mm
Take-off angle: 2.8°
Scan mode: θ–2θ
Maximum Bragg angle: 35°
Scan angle: $\Delta\theta = \Delta\theta_0 + B \tan\theta$; $\Delta\theta_0$ = 1°; B = 0.347
Values determining the scan speed:
SIGPRE = 0.66 SIGMA = 0.018
VPRE = 10°/mn TMAX = 80 s
Standard intensity reflexions: 100, 220, $2\bar{3}\bar{2}$ measured every 3600 s.
Independent recorded reflexions: 2626
Utilized reflexions: 1355 ($F_0^2 > 3\sigma(F_0^2)$)

for the sodium salt. These values combined with the measured densities are consistent with $Z = 1$ unit of formula $M_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ per cell. The presence of two water molecules per nickel atom was fully confirmed by the structure analysis.

X-ray Diffraction Measurements. Collection and Reduction of Data

A single crystal of each compound was mounted on a CAD-4 Enraf-Nonius, PDP8/M computer monitored diffractometer using MoK_α radiation monochromatized by an oriented graphite crystal. Accurate unit-cell constants were refined by optimizing the settling angles of 25 reflexions. They are reported along with data collection conditions in Table I for the lithium compound and in Table II for the sodium compound.

The collected reflections corresponded to Miller indices hkl, $hk\bar{l}$, $h\bar{k}l$ and $h\bar{k}\bar{l}$. The three standard reflexions showed no significant change. The data were processed [5] using an ignorance factor p of 0.03 for the lithium compound and 0.02 for the sodium compound, in the estimation of standard deviations. They were also corrected for absorption (Tables I and II).

The structures were solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques [5]. The quantity minimized is $\Sigma w(|F_0| - |F_c|)^2$ where $|F_0|$ and $|F_c|$ are the observed and calculated structure amplitudes put on the same scale, and the weight $w = 4F_0^2/\sigma^2(F_0^2)$. The reliability coefficients are defined as:

$$R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$$

$$R_w = (\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2)^{1/2}$$

The atomic scattering factors and anomalous terms are from the tabulation in [6].

Structures Solution

Both structures were refined in the same way. Space group $P\bar{1}$ was assumed, implying that the nickel atom to lie on a center of symmetry, the positions of the other non-hydrogen atoms being then readily observed in the tridimensional Patterson map. The anisotropic refinement of non-hydrogen atoms led to R factors of about 0.04. On a subsequent difference Fourier map, two peaks closely related to the oxygen atom O_w of the water molecule were attributed to hydrogen atoms. Their positions were introduced with isotropic thermal coefficients in the refinement, and two more cycles, including also Zacchariasen's secondary extinction parameter, were run. Then, the resulting hydrogen coordinates were corrected in such a way as to get $H–O_w$ bond lengths equal to 1 Å while keeping the angle $H–O_w–H$ equal to the value resulting from the previous refinement. In the next and last cylce, these new hydrogen coordinates and the corresponding isotropic thermal coefficients taken equal to 2 Å^2 in the case of the lithium compound and to 3 Å^2 in the case of the sodium compound were not varied. Final reliability factors were $R = 0.027$ and $R_w = 0.034$ for the 1712 observations and 80 variables in the case of $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$, and $R = 0.035$ and $R_w = 0.036$ for the 1355 observations and 80 variables in the case of $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$. The errors in an observation of unit weight were respectively 1.53 and 1.64 electrons. In both cases, the maximum shift per error in the last cycle was around 0.1, and a final difference Fourier map did not show peaks higher than 1/20 of peaks corresponding to a carbon atom in a Fourier map.

The final positional and thermal parameters are listed in Tables III and IV, and selected interatomic distances and bond angles in Tables V and VI. The listings of observed and calculated structure factors are available.

Description and Discussion of the Structures

Lithium and sodium bis(dithioxalato)nickelate(II) dihydrates are isostructural: their structures are made of anions $Ni(S_2C_2O_2)_2^{2-}$, alkali cations and water molecules, forming separate stacks parallel to the crystallographic c axis. Ball and spoke drawings of the structures parallel to plane (001) are given in Figs. 1a and 1b with numbering scheme of atoms. These structures will be discussed mainly in terms of comparison with those of black $K_2Ni(S_2C_2O_2)_2$ [2] and of red $K_2Ni(S_2C_2O_2)_2$ [7]. Features subjected to comparison are assembled in Tables VII and VIII.

The main feature of the two structures presented, like the one of black $K_2Ni(S_2C_2O_2)_2$, is the stacking of quasi-planar anions $Ni(S_2C_2O_2)_2^{2-}$, the nickel atom lying on a center of symmetry and being coordinated to two dithioxalate groups through the sulfur atoms located at the corners of a quasi-square parallelogram.

TABLE III. Positional and Thermal Parameters for the Atoms of $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$.

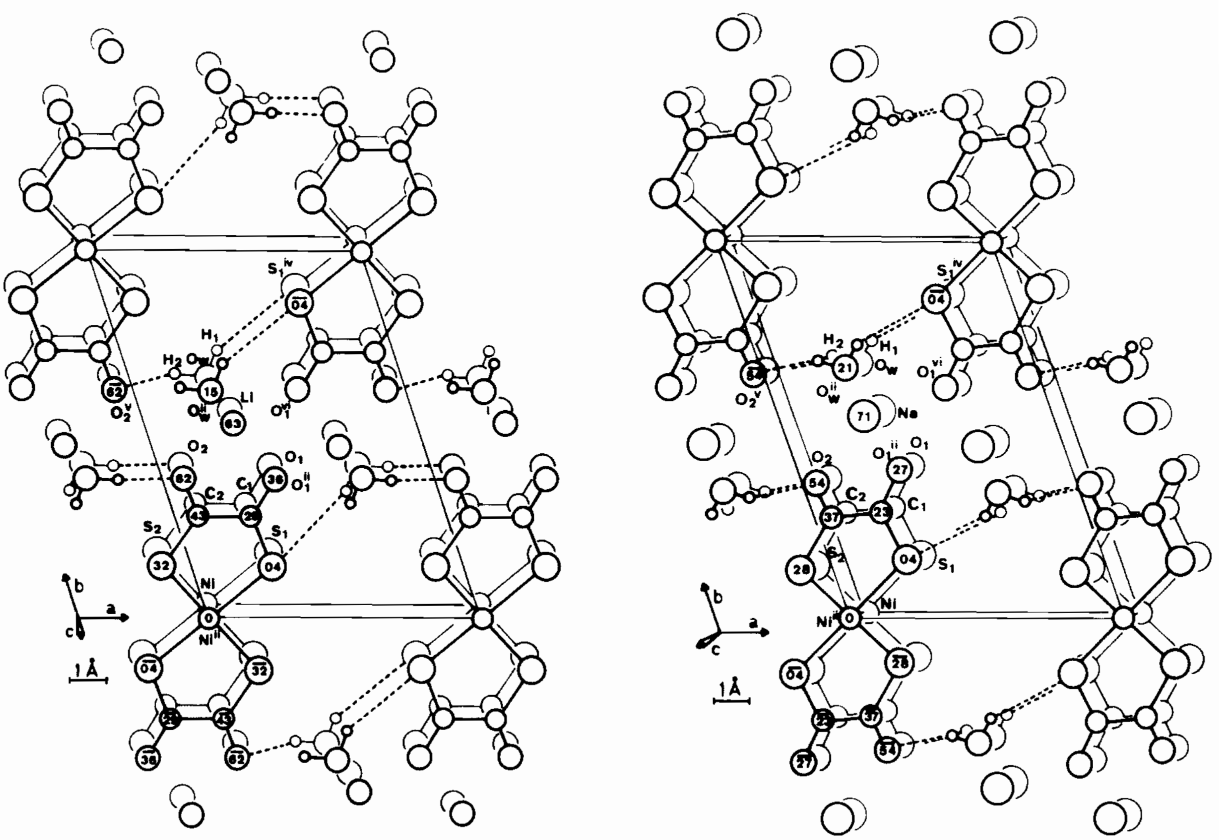
Atom	x	y	z	β_{11} or B(Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0	0	6.55(6)	2.60(3)	28.3(2)	−0.23(3)	0.89(8)	−2.27(6)
Li^+	0.3223(5)	0.5322(4)	0.635(1)	8.2(6)	4.6(3)	52(3)	1.1(3)	1(1)	−3.8(7)
S(1)	0.28799(6)	0.13730(4)	0.0383(1)	6.72(7)	3.06(4)	34.9(3)	0.36(4)	1.8(1)	−2.91(8)
S(2)	−0.11317(6)	0.14147(4)	0.3216(1)	6.08(7)	3.47(4)	39.4(3)	−0.11(4)	1.5(1)	−3.05(8)
O(1)	0.4012(2)	0.3783(1)	0.3591(4)	6.2(2)	3.5(1)	54(1)	−0.4(1)	0.8(4)	−4.6(3)
O(2)	0.0718(2)	0.3777(1)	0.6232(4)	8.1(2)	3.4(1)	47(1)	0.7(1)	3.6(4)	−4.0(3)
C(1)	0.2689(2)	0.2753(2)	0.2850(5)	5.9(3)	2.8(1)	26(1)	0.4(1)	0.1(4)	−1.0(3)
C(2)	0.0758(2)	0.2763(2)	0.4288(5)	6.8(3)	2.8(1)	26(1)	0.5(1)	1.3(4)	−0.4(3)
O_w	0.2776(3)	0.6185(2)	0.1542(5)	7.9(3)	5.0(1)	50(1)	1.6(2)	2.7(5)	−1.3(3)
H(1)	0.368	0.711	0.184	2					
H(2)	0.151	0.626	0.219	2					

Estimated standard deviations in the last significant figure(s) are given in parentheses, in this and subsequent Tables. The form of the anisotropic thermal ellipsoid is $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. The quantities given in the table are the thermal coefficients × 10^3.

TABLE IV. Positional and Thermal Parameters for the Atoms of $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$.

Atom	x	y	z	β_{11} or B(Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0	0	8.3(1)	2.96(5)	37.7(5)	0.48(6)	3.8(2)	−3.7(1)
Na^+	0.3105(2)	0.5347(1)	0.7128(4)	9.4(3)	3.8(1)	38(1)	−0.6(1)	5.6(4)	−5.4(3)
S(1)	0.2727(1)	0.15177(7)	0.0384(2)	8.5(1)	3.56(7)	48.2(6)	0.68(7)	5.7(2)	−4.2(2)
S(2)	−0.1233(1)	0.12119(7)	0.2750(2)	8.3(1)	3.75(7)	51.3(6)	0.47(7)	5.2(2)	−4.3(2)
O(1)	0.3623(3)	0.3903(2)	0.2659(6)	10.3(4)	3.6(2)	63(2)	−0.5(2)	5.8(7)	−5.1(5)
O(2)	0.0387(3)	0.3545(2)	0.5448(7)	11.7(5)	4.2(2)	73(2)	1.1(2)	8.3(8)	−8.4(5)
C(1)	0.2415(4)	0.2814(3)	0.2300(8)	9.3(6)	3.6(2)	32(2)	1.2(3)	1.8(9)	−1.9(5)
C(2)	0.0528(4)	0.2637(3)	0.3674(8)	9.7(6)	3.5(2)	38(2)	1.5(3)	2.4(9)	−2.0(6)
O_w	0.3021(5)	0.6628(3)	0.2113(8)	14.5(6)	6.8(3)	69(2)	4.4(4)	5.9(9)	−4.1(6)
H(1)	0.402	0.749	0.188	3					
H(2)	0.188	0.682	0.258	3					

For the thermal coefficients, see footnote of Table III.



(a) (b)

Fig. 1. Views of the structures of (a) $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ and (b) $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$, down the *c* axis.

These stacks develop along the crystallographic *c* axis with Ni–Ni spacings equal to *c*, *i.e.* 3.785(1) Å in the sodium compound and 3.666(1) Å in the lithium compound. As expected, these spacings are much shorter than in black $K_2Ni(S_2C_2O_2)_2$ where they amount to 4.1911(3) Å. The tilt angle ω of the normal to the plane of coordination of the nickel atom with the stacking axis, which is 34° in black $K_2Ni(S_2C_2O_2)_2$, is lowered to 30° in the sodium salt and to 28° in the lithium salt. Therefore the intrastack distance between the planes of coordination of two successive nickel atoms, which is 3.47 Å in black

TABLE V. Selected Interatomic Distances (Å) and Bond Angles (deg) in $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$.

Code of equivalent positions relative to x, y, z used in this and subsequent Tables:

i :	$\bar{x}, \bar{y}, \bar{z}$
ii :	x, y, 1 + z
iii :	x, y, $\bar{1}$ + z
iv :	1 – x, 1 – y, $\bar{z}$
v :	$\bar{x}$, 1 – y, 1 – z
vi :	1 – x, 1 – y, 1 – z
vii :	1 – x, 1 – y, 2 – z

Around Nickel:

Ni–S(1) :	2.190(1)
Ni–S(2) :	2.187(1)
Ni–S(2)^{iii} :	3.300(1)
Ni–Ni^{ii} :	3.666(1)
S(1)–Ni–S(2) :	92.42(4)
S(1)–Ni–S(2) :	94.28(4)
S(2)–Ni–S(2)^{iii} :	81.11(3)

Dithioxalate Group

S(1)–C(1) :	1.693(2)
S(2)–C(2) :	1.692(2)
C(1)–O(1) :	1.237(2)
C(2)–O(2) :	1.243(2)
C(1)–C(2) :	1.527(2)
S(1)–S(2) :	3.160(2)
S(1)–S(2)^{i} :	3.028(2)
S(1)–O(1) :	2.606(2)
S(2)–O(2) :	2.613(2)
O(1)–O(2) :	2.619(2)
Ni–S(1)–C(1) :	104.76(7)
Ni–S(2)–C(2) :	105.04(7)
S(1)–C(1)–C(2) :	119.0(1)
S(2)–C(2)–C(1) :	118.7(1)
S(1)–C(1)–O(1) :	124.9(1)
S(2)–C(2)–O(2) :	125.2(1)
O(1)–C(1)–C(2) :	116.1(2)
O(2)–C(2)–C(1) :	116.1(2)

Around Lithium:

Li–O(1)^{vi} :	1.989(4)
Li–O(2) :	2.063(4)
Li–O(1) :	2.077(4)
Li–O$_w$^{ii} :	2.096(4)
Li–O$_w$:	2.148(5)
Li–Li^{vi} :	3.067(7)
Li–Li^{ii} :	3.666(1)
Li–Li^{vii} :	4.110(8)

Water Molecule and Hydrogen Bonds:

O$_w$–H(1) = O$_w$–H(2) :	1
O$_w$–S(1)^{iv} :	3.553(3)
O$_w$–O(2)^{v} :	2.729(3)
H(1)–S(1)^{iv} :	2.71(4)
H(2)–O(2)^{v} :	1.74(4)
H(1)–O$_w$–H(2) :	107(3)
O$_w$–H(1)–S(1)^{iv} :	142(3)
O$_w$–H(2)–O(2)^{v} :	172(4)
S(1)^{iv}–O$_w$–O(2)^{v} :	135.4(1)
Li–O$_w$–Li^{iii} :	119.5(2)
Li–O$_w$–S(1)^{iv} :	106.1(1)
Li–O$_w$–O(2)^{v} :	93.7(1)
Li^{iii}–O$_w$–S(1)^{iv} :	83.2(1)
Li^{iii}–O$_w$–O(2)^{v} :	121.1(1)

TABLE VI. Selected Interatomic Distances (Å) and Bond Angles (deg) in $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$.

For the code of equivalent positions, see Table V.

Around Nickel:

Ni–S(1) :	2.176(1)
Ni–S(2) :	2.180(1)
Ni–S(2)^{iii} :	3.294(1)
Ni–Ni^{ii} :	3.785(1)
S(1)–Ni–S(2) :	92.02(3)
S(1)–Ni–S(2)^{iii} :	90.96(5)
S(2)–Ni–S(2)^{iii} :	84.91(3)

Dithioxalate Group:

S(1)–C(1) :	1.695(3)
S(2)–C(2) :	1.696(3)
C(1)–O(1) :	1.237(3)
C(2)–O(2) :	1.241(3)
C(1)–C(2) :	1.521(4)
S(1)–S(2) :	3.133(1)
S(1)–S(2)^{i} :	3.025(1)
S(1)–O(1) :	2.602(2)
S(2)–O(2) :	2.604(2)
O(1)–O(2) :	2.669(3)
Ni–S(1)–C(1) :	105.5(1)
Ni–S(2)–C(2) :	105.4(1)
S(1)–C(1)–C(2) :	118.2(2)
S(2)–C(2)–C(1) :	118.3(2)
S(1)–C(1)–O(1) :	124.3(2)
S(2)–C(2)–O(2) :	124.2(2)
O(1)–C(1)–C(2) :	117.4(2)
O(2)–C(2)–C(1) :	117.5(2)

Around Sodium:

Na–O(1)^{vi} :	2.352(3)
Na–O$_w$^{ii} :	2.363(3)
Na–O(2) :	2.373(3)
Na–O$_w$:	2.393(4)
Na–O(1) :	2.455(3)
Na–O(1)^{ii} :	2.739(3)
Na–Na^{vi} :	3.714(7)
Na–Na^{ii} :	3.785(1)
Na–Na^{vii} :	3.814(7)

Water molecule and Hydrogen bonds:

O$_w$–H(1) ≈ O$_w$–H(2) :	1
O$_w$–S(1)^{iv} :	3.400(3)
O$_w$–O(2)^{v} :	2.777(4)

(Continued overleaf)

TABLE VI. *(Continued)*

H(1)–S(1)^{iv}	: 2.57(6)
H(2)–O(2)^{v}	: 1.85(5)
H(1)–O$_w$–H(2)	: 105(5)
O$_w$–H(1)–S(1)^{iv}	: 141(6)
O$_w$–H(2)–O(2)^{v}	: 152(5)
S(1)^{iv}–O$_w$–O(2)^{v}	: 149.3(1)
Na–O$_w$–Na^{iii}	: 105.5(2)
Na–O$_w$–S(1)^{iv}	: 114.6(1)
Na–O$_w$–O(2)^{v}	: 82.1(1)
Na^{iii}–O$_w$–S(1)^{iv}	: 82.2(1)
Na^{iii}–O$_w$–O(2)^{v}	: 119.6(1)

$K_2Ni(S_2C_2O_2)_2$, is lowered to 3.28 Å in $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ and to 3.24 Å in $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$. In the same time the overlap between neighbouring anions $Ni(S_2C_2O_2)_2^{2-}$, which are quasi-planar entities (*vide infra*), is slightly enlarged. Taking into account that, in the three compounds, neighbouring groups $Ni(S_2C_2O_2)_2$ eclipse each other, the closest possible approach of two such groups is achieved in the lithium compound: indeed, in this compound, the stacking periodicity of 3.67 Å is exactly twice the van der Waals radius of sulfur (1.85 Å [8]).

The tilt angle ω is quite complementary of the angle Ni^{ii}–Ni–S [2] (Ni^{ii}–Ni is along the stacking axis), while the angle Ni^{ii}–Ni–S(1) is close to 90° (Table VII): this means that the anions $Ni(S_2C_2O_2)_2^{2-}$ are tipped nearly around Ni–S(1) bonds (Fig. 2). Consequently the nickel environment is completed into an elongated octahedron with two centrosymmetrically related sulfur atoms S(2) from neighbouring $Ni(S_2C_2O_2)_2$ groups, one above and one below, at distances Ni–S(2)^{ii} quite equal in both compounds: 3.300(1) Å in the lithium compound, and

TABLE VII. Compared Interatomic Distances (Å) and Angles (deg) in the Series of Potassium, Sodium and Lithium Bis(dithioxalate)Nickelate(II).

	$K_2Ni(dto)_2$ red	$K_2Ni(dto)_2$ black	$Na_2Ni(dto)_2$	$Li_2Ni(dto)_2$
Ni–S(1)	2.181(3)	2.1785(5)	2.176(1)	2.190(1)
Ni–S(2)	2.178(3)	2.1867(4)	2.180(1)	2.187(1)
S(1)–S(2)^{a}	3.160(3)	3.142(1)	3.133(1)	3.160(2)
S(1)–S(2)^{b}	3.033(4)^{c} 2.990(4)	3.030(1)	3.025(1)	3.028(2)
S(1)–C(1)	1.756(9)	1.712(2)	1.695(3)	1.693(2)
S(2)–C(2)	1.744(9)	1.701(2)	1.696(3)	1.692(2)
C(1)–C(2)	1.544(10)	1.540(3)	1.521(4)	1.527(2)
C(1)–O(1)	1.197(10)	1.230(2)	1.237(3)	1.237(2)
C(2)–O(2)	1.216(10)	1.238(2)	1.241(3)	1.243(2)
O(1)–O(2)	2.694(8)	2.702(2)	2.669(3)	2.619(2)
S(1)–O(1)	2.619(9)	2.603(2)	2.602(2)	2.606(2)
S(2)–O(2)	2.626(9)	2.607(1)	2.604(2)	2.613(2)
S(1)–Ni–S(2)^{a}	92.9(1)	92.09(2)	92.02(3)	92.42(4)
S(1)–Ni–S(2)^{b}	88.1(1)^{c} 86.7(1)	87.91(2)	87.98(3)	87.58(4)
Ni^{ii}–Ni–S(1)		56.49(2)	89.67(4)	87.62(4)
Ni^{ii}–Ni–S(2)		88.25(2)	60.09(3)	62.78(3)
ω		34	30	28
Ni–S(1)–C(1)	106.2(3)	105.9(7)	105.5(1)	104.76(7)
Ni–S(2)–C(2)	105.8(3)	105.9(6)	105.4(1)	105.04(7)
S(1)–C(1)–C(2)	116.7(8)	117.9(1)	118.2(2)	119.0(1)
S(2)–C(2)–C(1)	118.3(9)	118.1(1)	118.3(2)	118.7(1)
S(1)–C(1)–O(1)	124.0(9)	123.6(2)	124.3(2)	124.9(1)
S(2)–C(2)–O(2)	124.0(9)	124.2(1)	124.2(2)	125.2(1)
O(1)–C(1)–C(2)	119.3(10)	118.4(2)	117.4(2)	116.1(2)
O(2)–C(2)–O(1)	117.6(10)	117.7(2)	117.5(2)	116.1(2)

[a] S atoms from the same group $S_2C_2O_2$. [b] S atoms from the two different groups $S_2C_2O_2$ of an anion $Ni(S_2C_2O_2)_2^{2-}$. [c] In red $K_2Ni(S_2C_2O_2)_2$, the Ni atom has point symmetry 2.

TABLE VIII. Least-squares Planes in $Ni(S_2C_2O_2)_2^{2-}$: Atom-to-plane Distances (10^{-3} Å) and Dihedral Angles (deg) in Red $K_2Ni(S_2C_2O_2)_2$ (cpd. 1), Black $K_2Ni(S_2C_2O_2)_2$ (cpd. 2), $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ (cpd. 3) and $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ (cpd. 4). Values with an Asterik are for the Atoms Used in the Plane Calculations.

	Plane I				Plane II				Plane III			
Atom	cpd. 1	cpd. 2	cpd. 3	cpd. 4	cpd. 1	cpd. 2	cpd. 3	cpd. 4	cpd. 1	cpd. 2	cpd. 3	cpd. 4
Ni	0*	0*	0*	0*	−99	−20	−254	−69	−7	106	169	88
S(1)	0*	0*	0*	0*	−5*	0*	−0*	−1*	30	69	215	81
S(2)	0*	0*	0*	0*	−63	−56	−200	−68	−2*	1*	2*	2*
C(1)	−47	20	−100	−13	6*	−2*	0*	2*	−2*	1*	2*	2*
C(2)	−23	50	−3	16	−2*	0*	0*	−1*	6*	−2*	−5*	−6*
O(I)	−113	18	−248	53	−2*	1*	−0*	−1*	−47	−39	−151	−58
O(2)	−41	12	87	72	17	51	165	69	−2*	1*	2*	2*

Angle cpd.	Plane I–Plane II	Plane I–Plane III	Plane II–Plane III
1	2.9	1.2	1.9
2	1.1	3.0	2.4
3	6.9	4.5	8.1
4	1.9	2.3	3.1

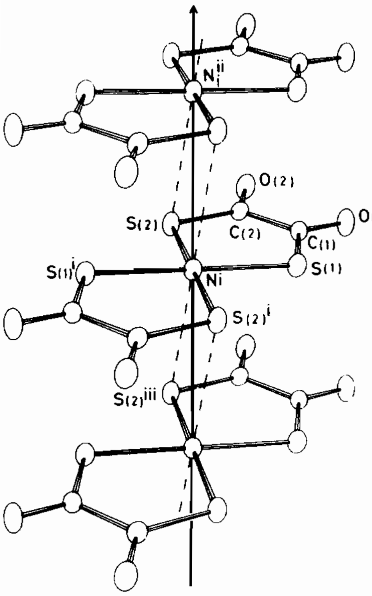


Fig. 2. Ortep drawing of stacking anions $Ni(S_2C_2O_2)_2^{2-}$ in $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$, illustrating the tipping of anions around Ni–S(1) and the elongated octahedron of sulfur atoms around Ni.

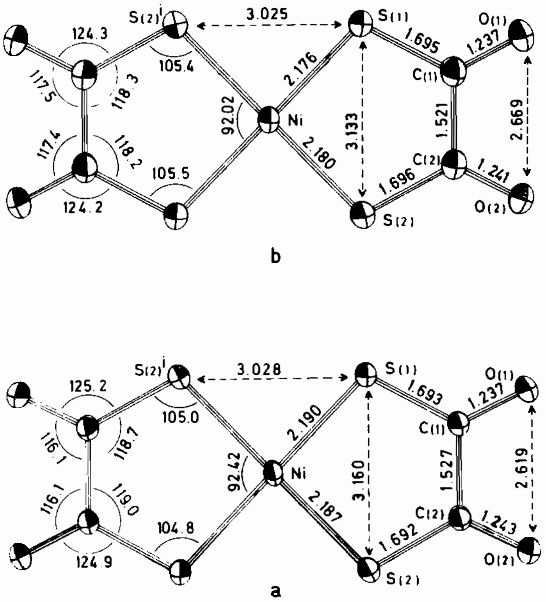


Fig. 3. Ortep drawings of the anion $Ni(S_2C_2O_2)_2^{2-}$ in (a) $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ and (b) $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$; the atoms are drawn at their 50% probability ellipsoids.

3.294(1) Å in the sodium compound. The same situation is encountered in black $K_2Ni(S_2C_2O_2)_2$ (Table VII), in which, however, the elongation of the octahedron is more important: Ni–S(1)^{ii} = 3.497(1) Å.

The geometry of the anion $Ni(S_2C_2O_2)_2^{2-}$ undergoes only minor changes from one compound to the other. Drawings of this anion in $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ and $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$, showing ellipsoids of atoms and relevant bond lengths and angles are presented in Fig. 3. The comparison of Ni–S bond lengths, S–S distances and S–Ni–S angles, in the planes of coordination of the nickel atoms, with those in black and red $K_2Ni(S_2C_2O_2)_2$ (Table VII), shows that chemically equivalent features are remarkably close to each other in the whole series, and that the little variations they exhibit from one compound to another may be related neither to the structure change nor to the cation.

Both compounds have dithioxalate groups exhibiting equal bonds C–S and equal bonds C–O within experimental error; these bonds have nearly the same lengths as in black $K_2Ni(S_2C_2O_2)_2$: at most one observes slight but not significant both shortening of C–S and lengthening of C–O when going from potassium to sodium and to lithium in the series of one-dimensional compounds. But, on the other hand, the red form of $K_2Ni(S_2C_2O_2)_2$, which does not correspond to a one-dimensional arrangement of anions $Ni(S_2C_2O_2)_2^{2-}$, presents C–S bonds 0.040 Å larger on the average and C–O bonds 0.025 Å shorter on the average than those in the one-dimensional compounds. Consequently the stacking of anions $Ni(S_2C_2O_2)_2^{2-}$ rather than the change of cation involves a weak increase of C–S bond order along with a weak decrease of C–O bond order. Whether the C–C bond order is affected to the same extent is more difficult to make sure: one observes a slight but not significant shortening of this bond in the sodium and in the lithium compounds (1.521(4) Å and 1.527(2) Å respectively) with respect to black $K_2Ni(S_2C_2O_2)_2$ (1.540(3) Å); but this latter value is not significantly shorter than that in red $K_2Ni(S_2C_2O_2)_2$ (1.544(10) Å).

The alkali cation exercises marked influence on the separation between oxygen atoms O(1) and O(2) because, in the four compounds, these atoms belong to its sphere of coordination. Very consistently, the distance O(1)–O(2) shortens strongly when going from potassium (2.694(9) Å in red $K_2Ni(S_2C_2O_2)_2$ and 2.702(2) Å in black $K_2Ni(S_2C_2O_2)_2$) to sodium (2.669(3) Å) and to lithium (2.619(2) Å). By the way the angles O–C–C decrease by about 2° while both angles S–C–O and angles S–C–C increase by about 1° in such a way that the sums of angles around carbon atoms are constantly equal to 360°, which indicates that atoms S(1), C(1), C(2), O(1) on one side, and S(2), C(2), C(1), O(2) on the other side, are coplanar in all four compounds.

The anion $Ni(S_2C_2O_2)_2^{2-}$ in $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ and in $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$, as well as in black and red $K_2Ni(S_2C_2O_2)_2$, departs only slightly from strict planarity. Deviations to planarity may be described in terms of dihedral angles between planes of atoms Ni, S(1), S(2), of atoms S(1), O(1), C(1), C(2) and of atoms S(2), O(2), C(2), C(1), in a moiety $Ni(S_2C_2O_2)$. Equations of these planes, atom-to-plane distances and angles between normals are given for the four compounds in Table VIII; the less planar $Ni(S_2C_2O_2)_2^{2-}$ appears in the sodium compound.

Unlike $K_2Ni(S_2C_2O_2)_2$, the lithium and sodium salts are hydrates. The water molecules are stacked in the same direction as anions $Ni(S_2C_2O_2)_2^{2-}$. Each water molecule is pseudotetrahedrally surrounded by two alkali cations, either Li at 2.096(4) Å and 2.148(5) Å, or Na at 2.363(3) Å and 2.393(3) Å, and by one oxygen atom, $O(2)^v$, and one sulfur atom, $S(1)^{iv}$, belonging to different dithioxalate groups (Fig. 4). These atoms are linked to the oxygen atom of water molecule by hydrogen bonds $O(2)^v \cdots H(2)–O_w$ and $S(1)^{iv} \cdots H(1)–O_w$ (Tables V, VI). As a matter of fact, the distances $H(1)–S(1)^{iv}$ and $H(2)–O(2)^v$, which measure respectively 2.71(4) Å and 1.74(4) Å in the lithium salt, and 2.57(6) Å and 1.85(5) Å in the sodium salt, are markedly shorter than the sums of van der Waals radii (r_H = 1 Å; r_O = 1.40 Å; r_S = 1.85 Å [8*]). Two water molecules bridge two units $Ni(S_2C_2O_2)_2$ related one to the other through the translation $\vec{a}-\vec{c}$ (Fig. 1).

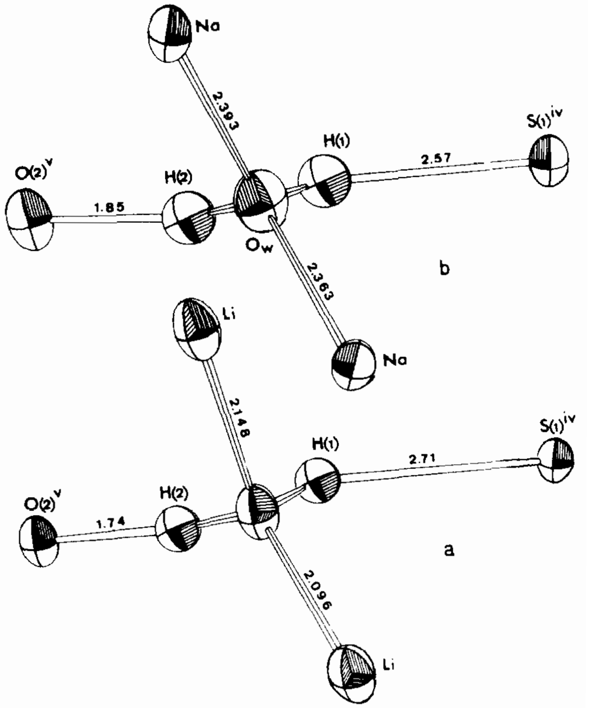


Fig. 4. The water molecule in (a) $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ and (b) $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$.

The environment of the alkali cations differs from one compound to the other. The lithium atom is surrounded by five oxygen atoms, two from water molecules and three from dithioxalate groups, at distances ranging from 1.989(4) Å to 2.148(5) Å, the next neighbouring oxygen or sulfur atoms being at more than 3.4 Å. An analysis of the dihedral angles according to the 'points on a sphere' method proposed by Kouba and Wreford [9] shows that the symmetry of the lithium environment is nearly half-

---

*The value of r_H = 1 Å, deduced from recent neutron diffraction studies is preferred to that of 1.2 Å given by Pauling [8].

TABLE IX. Dihedral Angles Analysis of the Closest Fivefold Environment by Oxygen Atoms of Li and Na in $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ and $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$. Measured Angles are Compared to Those Calculated for Both Trigonal-bipyramidal (TBP) and Square-pyramidal (SP) Ideal Geometries.

Dihedral	Ideal TBP	$Li_2Ni(dto)_2$	$Na_2Ni(dto)_2$	Ideal SP
$O(1)^{vi}$–O(1)	101.5	108.2	119.4	119.8
$O(1)^{vi}$–O_w	101.5	85.3	70.8	75.7
$O(1)^{vi}$–O_w^{ii}	101.5	115.8	126.1	119.8
O(2)–O(1)	101.5	110.1	125.3	119.8
O(2)–O_w	101.5	83.6	72.2	75.7
O(2)–O_w^{ii}	101.5	116.1	125.7	119.8
O(1)–O_w	53.1	64.6	65.4	75.7
O_w–O_w^{ii}	53.1	70.5	86.3	75.7
O_w^{ii}–O(1)	0	19.8	6.9	75.7

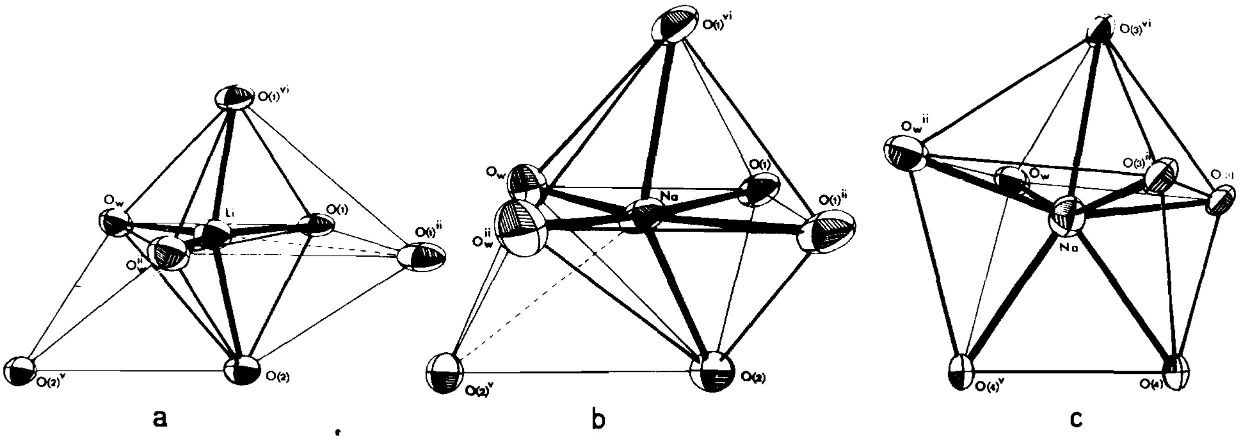


Fig. 5. The polyhedron of coordination of the alkali cation in (a) $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$, (b) $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ and (c) $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$.

way between trigonal bipyramidal and square pyramidal with Li–O_w as pseudo-fourfold axis of the square pyramid (Table IX, Fig. 5a).

Around the sodium atom, one finds again the same five oxygen atoms as in the case of lithium, at distances ranging from 2.352(3) Å to 2.455(3) Å, and located at the corners of a quasi-square pyramid with Na–O_w as pseudo-fourfold axis, as shown from the dihedral angles analysis reported in Table IX. However, the larger size of the cation allows the build up of a sixth contact, namely with oxygen atom $O(1)^{ii}$ which stands at 2.793(3) Å. This distance is a little larger than the five previous ones, but markedly shorter than those of next neighbouring atoms which amount to more than 3.4 Å. This sixth oxygen atom completes the sodium environment into an irregular octahedron (Fig. 5b).

Then both these structures appear as packings of parallel thick layers of infinite ribbons $[Ni(S_2C_2O_2)_2 \cdot (H_2O)_2]_n$ running along $\vec{a}-\vec{c}$. These ribbons are held together by the alkali cations.

It is most interesting to put side by side these structures and that of the homologous sodium bis(oxalato)cuprate(II) dihydrate, $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$, which exhibits the same structural features [10] *i.e.*: a triclinic cell of nearly the same dimensions and separate stacks of planar $Cu(C_2O_4)_2^{2-}$ anions, of Na^+ cations and of water molecules, all parallel to the shortest cell axis, *c* (Fig. 6). However, due to a larger tilt angle ω of anions $Cu(C_2O_4)_2^{2-}$ on the stacking axis ($\omega = 39°$) and to the smaller size of oxygen atom compared to sulfur, the water molecule in $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$ may accommodate a higher coordinate y (y = 0.75) than in the bis(dithioxalato)nickelates (y = 0.62 and 0.65). It results that in $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$, the hydrogen bonds, either H(1)···O(1) or H(2)···O(2), do not concern non coordinating oxygen atoms of oxalate groups, but are directed exclusively towards coordinating ones (Fig. 6); moreover, they connect anions $Cu(C_2O_4)_2^{2-}$ which are related through the translation $\vec{a}$. The resulting lower value of parameter *b* (9.47 Å instead of 10.64 Å and 11.05 Å) enables the sodium atom to be in close contact with seven oxygen atoms, two from water molecules and five from oxalate groups, at distances ranging from 2.37 Å to 2.59 Å, located at

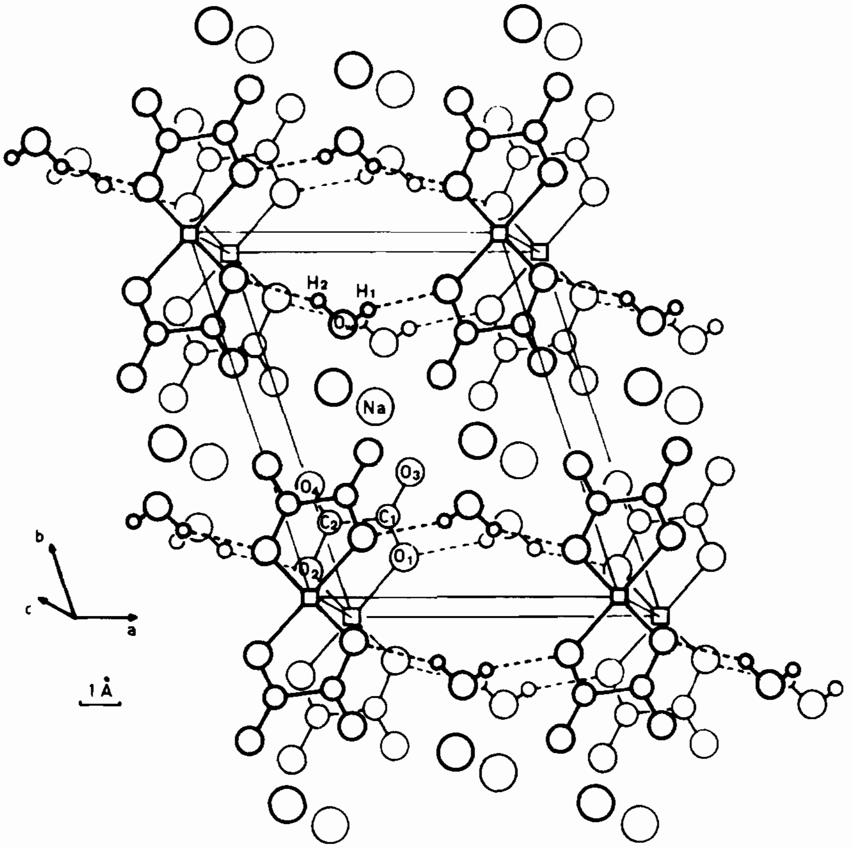


Fig. 6. View of the structure of $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$ down the *c* axis.

the corners of an irregular monocaped trigonal prism; six of these oxygen atoms are equivalent in position to those around Na in $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$. Therefore, when going from $Na_2Cu(C_2O_4)_2 \cdot 2H_2O$ to $Na_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$ and to $Li_2Ni(S_2C_2O_2)_2 \cdot 2H_2O$, the number of coordination of the alkali cation decreases from 7 to 6 and to 5, under the conjugated influences of a rearrangement of hydrogen bonds array, of size of cation and of variations of cell parameters, especially an increase of *b* and changes in angles. This evolution is illustrated in Fig. 5.

Acknowledgements

This work has been technically supported in part by the C.N.R.S., the D.G.R.S.T. and the D.E.S.R. We thank Dr. J. Galy for helpful discussions.

References

1 Presented at the *Vth European Crystallographic Meeting*, Copenhagen (1979); Abstract no. 15-P3-2.

2 A. Gleizes, F. Clery, M. F. Bruniquel and P. Cassoux, *Inorg. Chim. Acta, 37,* 19 (1979).

3 C. S. Robinson and H. O. Jones, *J. Chem. Soc., 101,* 62 (1912); E. G. Cox, W. Wardlaw and K. C. Webster, *ibid.,* 1475 (1935).

4 For a good review of works on partially oxidized $Pt(C_2O_4)_2^{2-}$, see J. S. Miller and A. Epstein, *Prog. Inorg. Chem., 20,* pp. 72–75 (1976).

5 In addition to local programs for the CII-IRIS 80, local modifications of the following programs were employed: Ibers' AGNOSTC program for absorption corrections, Zalkin's FORDAP Fourier program, Ibers and Doedens' NUCLS least-squares program, Busing and Levy's ORFLS program and Johnson's ORTEP II program.

6 D. T. Cormer and J. T. Waber, 'International Tables for X-ray Crystallography', Vol. IV, Table 2.2 A, Kynoch Press, Birmingham (1974); D. T. Cromer, *ibid.,* Table 2.3.1.

7 D. Coucouvanis, N. C. Baezinger and S. M. Johnson, *J. Am. Chem. Soc., 95,* 3875 (1975).

8 L. Pauling, 'The Nature of the Chemical Bond', 3rd Edn., Cornell University Press, Ithaca, N.Y. (1960).

9 J. K. Kouba and S. S. Wreford, *Inorg. Chem., 15(6),* 1643 (1976).

10 A. Gleizes, F. Maury and J. Galy, *Inorg. Chem.,* in press.