Volume 20
Number 12
December 1981

Inorganic Chemistry

Contribution from the Department of Chemistry,
University of New Mexico, Albuquerque, New Mexico 87131

Crystal Structure of Disodium *fac*-Tris(glycinato)nickelate(II) Perchlorate Hydrate-d_2, $Na_2[Ni(NH_2CH_2COO)_3]ClO_4 \cdot D_2O$

CHARLES F. CAMPANA,* DONALD F. SHEPARD, and WILLIAM M. LITCHMAN

Received March 21, 1980

The crystal structure of disodium *fac*-tris(glycinato)nickelate(II) perchlorate hydrate-d_2, $Na_2[Ni(NH_2CH_2COO)_3]ClO_4 \cdot D_2O$, has been determined by single-crystal X-ray diffraction techniques. The complex crystallizes in the monoclinic space group $C2/c$ with a cell of dimensions a = 15.889 (5) Å, b = 8.929 (3), Å c = 22.961 (9) Å, β = 100.08 (3)°, and Z = 8. The calculated density is 1.84 g/cm^3 compared to the observed density of 1.83 (2) g/cm^3. Scintillation-counter diffractometry was used to measure the intensities of 3709 independent reflections for $2\theta \le 55°$ of which 3226 reflections were considered observed with $I \ge 2\sigma(I)$. The phase problem was solved by the application of direct methods, and the structural parameters were refined by full-matrix least-squares procedures to final R_F = 5.5 and R_{wF} = 5.7. Anisotropic thermal parameters were used for all atoms except hydrogen. The nickel atom is octahedrally coordinated to the three glycinato ligands such that the three nitrogen atoms are mutually cis. Average bond lengths are as follows (Å): Ni–N, 2.091 (4); Ni–O, 2.050 (9); N–C, 1.446 (4); C–C, 1.516 (5); C–O(coordinated), 1.264 (3); C–O(carbonyl), 1.238 (9). The individual cations and anions in the crystal are held together by a three-dimensional network of strong hydrogen bonds and Na···O interactions.

Introduction

The interactions between metals and amino acids and peptides are of considerable interest as coordination phenomena, as models for metal–protein reactions, and as models for biological systems in which the properties of proteins are modified by the fact that metal atoms are attached to them.[1] The formation of amino acid complexes of nickel(II) has been extensively studied.[1-3] Although both 1:2 and 1:3 complexes of nickel(II) with amino acids can be prepared in solution, detailed X-ray crystallographic studies have only been reported for the bis complexes.[3-7] We report here the results of an accurate three-dimensional X-ray crystallographic analysis of the structure of disodium *fac*-tris(glycinato)nickelate(II) perchlorate hydrate-d_2, $Na_2[Ni(NH_2CH_2COO)_3]ClO_4 \cdot D_2O$.

Experimental Section

The complex was prepared by dissolving $NiCl_2 \cdot 6D_2O$ (1.2 mmol) and glycine (0.4 mmol) in a 2.0-mL solution of D_2O–NaOD (99.8% enrichment). The solution was slowly acidified by the addition of $DClO_4$ to pH 5.0. The solution was allowed to stand, slowly evaporating, for several months at room temperature during which time two different types of crystals formed. The blue crystals have been shown by this X-ray analysis to contain the facial isomer of $Ni(Gly)_3^-$, while the green crystals are thought to contain the meridional isomer.[8]

A needle-shaped blue crystal of approximate dimensions 0.20 × 0.40 × 0.20 mm was selected for the structural analysis. The specimen was glued to the tip of a thin glass fiber and seated into a brass pin on an eucentric goniometer with the use of beeswax and epoxy cement. The goniometer was mounted on a Nicolet P3/F four-circle automated diffractometer under the control of a Data General Nova 3/12 computer with 32K or 16-bit word memory, a Data General disk unit of 5.0 × 10^6 16-bit words, a 9-track tape drive, and a Qume printer.

Since this is the first structural study performed by this research group using this instrument, experimental techniques will be described in detail. This description will then be referenced in future reports from our laboratory.

The diffractometer was equipped with a molybdenum-target X-ray tube [λ(Mo Kα_1) 0.709 300 Å, λ(Mo Kα_2) 0.713 590 Å, λ(Mo K$\bar{\alpha}$) 0.710 730 Å],[9] operated at 50 kV and 20 mA, and a highly oriented graphite crystal monochromator mounted with equatorial geometry.

The crystal was centered in a random orientation. Determination of the crystal orientation, unit cell parameters, and crystal quality was accomplished by the following procedure.[10]

(1) A random-orientation rotation photograph was taken with $2\theta = \omega = \chi = 0°$ with the ϕ axis rotating at 234°/min for 20 min. The

---

[1] Freeman, H. C. *Inorg. Biochem.* **1973**, *1*, 121–166.

[2] (a) Ahmed, A. K. S.; Wilkins, R. G. *Proc. Chem. Soc.* **1959**, 399. (b) *J. Chem. Soc. London* **1960**, 2895. (c) *Ibid.* **1960**, 2901. (d) Lim, M. C.; Nancollas, G. H. *Inorg. Chem.* **1971**, *10*, 1957. (e) Margerum, D. W.; Rosen, H. M. *Ibid.* **1969**, *8*, 1535. (f) Eigen, M. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 753. (g) Kustin, K.; Pasternack, R. F.; Weinstock, E. M. *J. Am. Chem. Soc.* **1966**, *88*, 4610. (h) Hammes, G. G.; Steinfield, J. I. *Ibid.* **1962**, *84*, 4639. (i) Cassatt, J. C.; Wilkins, R. G. *Ibid.* **1968**, *90*, 6045. (j) Ahmed, A. K. S.; Wilkins, R. G. *J. Chem. Soc.* **1959**, 3700. (k) Margerum, D. W.; Rorabacher, D. B.; Clarke, J. F. G., Jr. *Inorg. Chem.* **1963**, *2*, 667. (l) McAuliffe, C. A.; Vallarino, L. M.; Quagliano, J. V. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 625.

[3] Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 257.

[4] Freeman, H. C.; Guss, J. M. *Acta Crystallogr., Sect. B* **1968**, *B24*, 1133.

[5] Van der Helm, D.; Hossain, M. B. *Acta Crystallogr., Sect. B* **1969**, *B25*, 457.

[6] Freeman, H. C.; Guss, J. M. *Acta Crystallogr., Sect B* **1972**, *B28*, 2090.

[7] Freeman, H. C.; Guss, J. M. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2451.

[8] Shepard, D. F., Ph.D. Dissertation, University of New Mexico, May 1979.

[9] Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 1.1A, p 8.

[10] Programs used for centering of reflections, autoindexing, refinement of cell parameters, axial photographs, and data collection are those described in: "Nicolet P3/R3 Data Collection Manual"; Calabrese, J. C., Ed.; Nicolet XRD Corp.: Cupertino, CA, 1980.

0020-1669/81/1320-4039$01.25/0 © 1981 American Chemical Society

Table I. Experimental Data for the X-ray Diffraction Study on Crystalline $Na_2[Ni(NH_2CH_2COO)_3]ClO_4 \cdot D_2O$

(A) Crystal Parameters at 27 °C

crystal system: monoclinic
space group: *C*2/*c*
a = 15.889 (5) Å
b = 8.929 (3) Å
c = 22.961 (9) Å
β = 100.08 (3)°
V = 3207.3 (18) Å^3
Z = 8
mol wt = 444.8
$F(000)$ = 304
ρ(calcd) = 1.84 g/cm^3
ρ(obsd)[a] = 1.83 g/cm^3

(B) Measurement of Intensity Data

diffractometer: Nicolet P3/F
radiation: Mo Kα ($\bar{\lambda}$ = 0.710 69 Å)
monochromator: highly oriented graphite crystal
reflctns measd: $+h,+k,\pm l$
2θ range: 3–55°
scan type: θ–2θ
scan speed: 3.91–29.3°/min (in 2θ)
scan range: $[2.0 + \Delta(\alpha_2 - \alpha_1)]°$
bkgd measment: stationary crystal and counter; at beginning and end of 2θ scan—each for half the time taken for 2θ scan
std reflctns: 2 measured every 48 reflections [350, 406]; no significant changes in intensity were observed
reflctns collected: 4092 total, yielding 3709 independent reflctns
reflctns obsd ($I > 2\sigma(I)$): 3226 (87%)
abs coeff: 14.9 cm^{-1}; emperical absorption correction made on the basis of ψ scans

[a] Measured by neutral buoyancy flotation method.

Table II. Positional Parameters with Esd's[a] for $Na_2[Ni(NH_2CH_2COO)_3]ClO_4 \cdot D_2O$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ni	0.36496 (2)	0.26319 (4)	0.36823 (2)
N(1)	0.3760 (2)	0.4609 (3)	0.3214 (1)
N(2)	0.2426 (2)	0.2010 (3)	0.3264 (1)
N(3)	0.4381 (2)	0.1267 (3)	0.3221 (1)
O(1)	0.4738 (1)	0.3432 (2)	0.4195 (1)
O(2)	0.5577 (1)	0.5431 (2)	0.4349 (1)
O(3)	0.2955 (1)	0.3717 (3)	0.4225 (1)
O(4)	0.1660 (2)	0.3944 (3)	0.4456 (1)
O(5)	0.3749 (1)	0.0771 (2)	0.4221 (1)
O(6)	0.4504 (2)	−0.1279 (3)	0.4454 (1)
C(1)	0.4963 (2)	0.4739 (3)	0.4072 (1)
C(2)	0.2164 (2)	0.3447 (3)	0.4143 (1)
C(3)	0.4295 (2)	−0.0191 (3)	0.4131 (1)
C(4)	0.4433 (2)	0.5527 (4)	0.3543 (2)
C(5)	0.1813 (2)	0.2436 (5)	0.3628 (2)
C(6)	0.4717 (3)	0.0027 (5)	0.3596 (2)
H(1)	0.3229	0.5147	0.3162
H(2)	0.3898	0.4372	0.2834
H(3)	0.2404	0.0945	0.3204
H(4)	0.2291	0.2507	0.2888
H(5)	0.4844	0.1837	0.3115
H(6)	0.4027	0.0891	0.2869
H(7)	0.4175	0.6397	0.3684
H(8)	0.4810	0.5828	0.3280
H(9)	0.1600	0.1541	0.3783
H(10)	0.1351	0.2953	0.3384
H(11)	0.5315	0.0202	0.3732
H(12)	0.4644	−0.0873	0.3364
Na(1)	0.57246 (8)	0.75328 (12)	0.49282 (6)
Na(2)	0.17886 (10)	0.61151 (16)	0.51068 (8)
Cl	0.31175 (7)	0.25964 (10)	0.17461 (4)
O(7)	0.2490 (2)	0.3446 (5)	0.1988 (2)
O(8)	0.3937 (2)	0.3242 (5)	0.1967 (2)
O(9)	0.2938 (4)	0.2605 (6)	0.1132 (2)
O(10)	0.3106 (2)	0.1126 (4)	0.1984 (2)
O(11)	0.6788 (2)	0.3718 (3)	0.5051 (1)
D(1)	0.639 (2)	0.408 (4)	0.529 (2)
D(2)	0.683 (3)	0.433 (6)	0.520 (2)

[a] Esd's, shown in parentheses, are right justified to the least significant digit of the preceding number. They are derived from the inverse of the final least-squares matrix.

photograph was recorded on a flat Polaroid film cassette mounted 97.5 mm from the crystal.

(2) Film separations ($2x_i$, $2y_i$) of 25 quartets of reflections were converted into diffractometer coordinates for individual reflections (i.e., 2θ and χ were directly calculated, ω was defined as 0°, and ϕ was determined by rotating the crystal until a peak of intensity greater then 10^3 counts/s was encountered) and were centered by an automated routine.

(3) The three shortest independent reciprocal vectors from step 2 were used to generate, by linear combinations, real-space vectors as possible unit cell axes from which the smallest, primitive cell was chosen by an auto-indexing routine to assign mutual indices to the 25 reflections. An automatic cell search routine transformed this cell to a C-centered monoclinic unit cell.

(4) Axial photographs were taken about each of the three axes chosen in step 3, with use of the Polaroid cassette attached to the diffractometer. The *m* symmetry about the *b* axis was confirmed, and all three axes selected above were found, by inspection, to be true solutions (rather than submultiples of the true axial lengths).

(5) The 25 reflections were assigned indices consistent with the unit cell selected in step 3, and the unit cell parameter and orientation matrix were calculated via least-squares techniques.

(6) All data in the angular range $30° < 2\theta < 35°$ were collected at the maximum scan rate (29.3°/min). From these data, 25 strong reflections, well dispersed in reciprocal space, were selected for least-squares refinement. Their 2θ, ω, and χ settings were determined via an automatic centering routine. These values were used in the least-squares refinement of cell parameters and orientation parameters. (Because of dispersion by the diffractometer, the Kα_1 and Kα_2 components were not resolved. The wavelength of Mo K$\bar{\alpha}$ radiation was used in determining cell constants.)

(7) Both θ–2θ and ω scans were recorded graphically for reflections along each of the principal reciprocal axes in order to determine the quality of the peak profiles and their spread in ω under standard operating conditions. All were found to be satisfactory.

(8) Several low-order reflections were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from $\psi = 0°$ to $\psi = 350°$. These reflections were then utilized to apply an empirical absorption correction to all data.

(9) Intensity data were collected via a θ(crystal)–2θ(counter) scan in 96 steps using bisecting geometry. The scan was from $[2\theta(\text{Mo K}\alpha_1) - 1.0]°$ to $[2\theta(\text{Mo K}\alpha_2) + 1.0]°$. A variable scan rate was employed in which a 1-s peak count measurement at the center of the scan range was used to select a scan rate from 3.92 to 29.3°/min for the actual data collection. Any step of the scan which exceeded 5000 counts was subjected to a linear correction for coincidence losses. A brass foil attenuator (attenuation factor ca. 100) was automatically inserted for all reflections exceeding 100 000 counts. Backgrounds (B_1 and B_2) were measured both at the beginning and at the end of the scan, each for half the time of the scan. The stability of the entire assembly was monitored by measuring two strong check reflections after every 48 data points. No significant changes were found. The intensity (I) and its standard deviation ($\sigma(I)$) were calculated from eq 1 and 2, where SC is the count during the scan and τ is the ratio of the scan

$$I = \text{SC} - \tau(B_1 + B_2) \tag{1}$$

$$\sigma(I) = [\text{SC} + \tau^2(B_1 + B_2)]^{1/2} \tag{2}$$

time to background time (1.0 in the present study). For all reflections for which $I < 0.698\sigma(I)$, I was reset to 0.698 $\sigma(I)$.

(10) The unscaled structure factor amplitude $|F_o|$ is given by $|F_o| = (I/Lp)^{1/2}$. Its standard deviation, $\sigma(F)$, was calculated as in eq 3. The Lp factor for a monochromator in equatorial mode is given

$$\sigma(F) = \sigma(I)/2Lp|F_o| \tag{3}$$

by eq 4. This equation assumes that the graphite monochromator

$$Lp = \frac{0.5}{\sin 2\theta}\left[\left(\frac{1 + (\cos^2 2\theta_m)(\cos^2 2\theta)}{1 + \cos^2 2\theta_m}\right) + \left(\frac{1 + |\cos 2\theta_m| \cos^2 2\theta}{1 + |\cos 2\theta_m|}\right)\right] \tag{4}$$

crystal is 50% mosaic and 50% perfect. The monochromator angle, $2\theta_m$, is 12.2° for Mo Kα radiation.

Table III. Anisotropic Thermal Parameters[a] with Esd's for $Na_2[Ni(NH_2CH_2COO)_3]ClO_4{\cdot}D_2O$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	1.85 (2)	1.45 (1)	2.10 (2)	−0.02 (1)	0.27 (1)	−0.13 (1)
N(1)	2.9 (1)	2.1 (1)	2.5 (1)	0.0 (1)	−0.2 (1)	−0.4 (1)
N(2)	2.3 (1)	2.9 (1)	2.8 (1)	−0.4 (1)	0.3 (1)	−0.9 (1)
N(3)	2.9 (1)	2.7 (1)	2.8 (1)	0.3 (1)	0.8 (1)	0.1 (1)
O(1)	2.3 (1)	2.0 (1)	2.7 (1)	−0.4 (1)	0.0 (1)	0.3 (1)
O(2)	2.7 (1)	2.1 (1)	3.9 (1)	−0.5 (1)	−0.3 (1)	−0.4 (1)
O(3)	2.3 (1)	2.5 (1)	3.0 (1)	−0.2 (1)	0.5 (1)	−0.9 (1)
O(4)	3.2 (1)	2.6 (1)	4.8 (1)	−0.4 (1)	2.1 (1)	−0.6 (1)
O(5)	2.6 (1)	1.7 (1)	3.0 (1)	0.3 (1)	0.9 (1)	0.2 (1)
O(6)	3.5 (1)	2.7 (1)	4.8 (1)	0.8 (1)	1.2 (1)	1.4 (1)
C(1)	2.1 (1)	1.8 (1)	2.7 (1)	0.0 (1)	0.4 (1)	−0.2 (1)
C(2)	2.5 (1)	1.7 (1)	3.1 (1)	−0.1 (1)	1.0 (1)	−0.1 (1)
C(3)	2.2 (1)	1.8 (1)	3.5 (1)	−0.1 (1)	0.5 (1)	0.1 (1)
C(4)	4.4 (2)	2.1 (1)	4.3 (2)	−1.0 (1)	−1.3 (1)	0.9 (1)
C(5)	2.4 (1)	5.3 (2)	4.5 (2)	−1.2 (1)	1.0 (1)	−2.1 (1)
C(6)	4.7 (2)	3.5 (2)	4.3 (2)	2.1 (1)	2.3 (1)	1.0 (1)
Na(1)	2.90 (5)	1.93 (5)	2.54 (5)	−0.24 (4)	0.61 (4)	−0.03 (3)
Na(2)	3.97 (7)	2.12 (6)	7.07 (10)	−0.48 (5)	2.89 (7)	−0.54 (6)
Cl	4.51 (4)	3.95 (4)	2.66 (3)	−0.84 (3)	0.11 (3)	0.04 (3)
O(7)	5.8 (2)	6.9 (2)	7.3 (2)	2.0 (2)	1.7 (2)	1.2 (2)
O(8)	4.9 (2)	6.6 (2)	5.5 (2)	−2.1 (1)	1.1 (1)	−0.9 (1)
O(9)	12.2 (4)	11.6 (4)	2.3 (1)	−3.3 (3)	−0.3 (2)	0.2 (2)
O(10)	7.3 (2)	4.0 (2)	6.0 (2)	−0.9 (1)	−0.2 (1)	0.4 (1)
O(11)	3.1 (1)	2.3 (1)	3.4 (1)	0.4 (1)	−0.1 (1)	−0.5 (1)

[a] The anisotropic thermal parameter is defined by the following expression $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. All hydrogen atoms were assigned a fixed isotropic temperature factors of 5.0 Å^2.

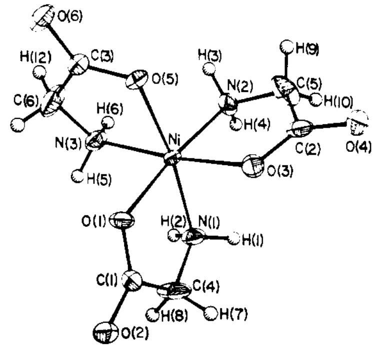


Figure 1. View of the *fac*-tris(glycinato)nickelate(II) anion showing the numbering scheme adopted for the atoms. Thermal ellipsoids are drawn at the 50% probably level, with hydrogen atoms shown as spheres of arbitrary size.

(11) An examination of the data set revealed systematic absences $h0l$ for $l = 2n + 1$ and hkl for $h + k = 2n + 1$, consistent with the space group $C2/c$. The systematically absent reflections were rejected. Numerical information of data collection is given in Table I.

Solution and Refinement of the Structure

All calculations were carried out on a Nicolet R3/XTL structure determination system.[11] The hardware on the XTL console consisted of a Data General Nova 3/12 computer with 32K of 16-bit word memory and a hardware floating point processor, a Data General disk unit with 5×10^6 16-bit words of storage, a 9-track tape drive, a Qume printer, a Versatec 1100/A printer/plotter, a Tektronix 4012 graphics terminal, and a Tektronix 4662 interactive digital plotter.

Scattering factors for nickel, chlorine, sodium, carbon, nitrogen, and oxygen were taken from the compilation of Cromer and Waber,[12] while those for hydrogen were taken from Stewart et al.[13] Both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms, with use of the values of Cromer and Liberman.[14]

All least-squares refinements were based upon the minimization of $\sum w(|F_o| - |F_c|)^2$ with use of counter weights, where $w = [\sigma_F{}^2 + (CF_o)^2]^{-1}$ with $C = 0.050$. Discrepancy indices used in the text are defined in eq 5 and 6. The "goodness of fit" (GOF) is defined in eq 7 wherein NO is the number of observations and NV is the number of variables.

$$\%\ R_F = 100[\sum||F_o| - |F_c||/\sum|F_o|] \qquad (5)$$

$$\%\ R_{wF} = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \qquad (6)$$

$$\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2} \qquad (7)$$

The structure was solved by direct methods using the program MULTAN.[15] Normalized structure factor amplitudes, $|E(hkl)|$, were generated from $|F_o(hkl)|$ values with the use of eq 8. Here the

$$|E(hkl)| = |F_o(hkl)|[\epsilon \sum_{j=1}^{j=N} f^2[j, \theta(hkl)]]^{-1/2} \qquad (8)$$

summation is over all N atoms in the unit cell, $|E(hkl)|^2$ is normalized by a scale factor $f[j, \theta(hkl)]$ in the scattering factor for the jth atom at the Bragg angle $\theta(hkl)$, and ϵ is a coefficient which corrects for the effects of space group symmetry. The statistical distribution of $|E|$ values was consistent with that expected for a centrosymmetric crystal.

The origin of the unit cell was defined by assigning zero phases to two strong reflections of appropriate parity (1,3,4, $|E| = 3.35$; 4,2,3, $|E| = 2.84$). Three additional strong reflections of differing parity and many $\sum_2$ interactions (1,1,5, $|E| = 2.48$; 1,7,10, $|E| = 3.62$; 6,4,−2, $|E| = 3.30$) were included in the starting reflection set. Application of the tangent formula by MULTAN-generated phases for 450 reflections with $|E| > 1.25$. Assignments of real (0 or 180°) phases to the starting reflections provided eight solutions. An E map generated from the phase set with the best combined figure of merit (2.97) yielded a chemically reasonable solution from which the coordinates of nickel, chlorine, and sodium atoms could be ascertained. Subsequent Fourier

---

(11) Programs used for data reduction, Fourier syntheses, block-diagonal and full-matrix least-squares refinement, bond length and bond angle calculations, error analysis, least-squares planes calculations, direct-methods structure solution, and calculation of hydrogen atom positions are those described in: "Nicolet P3/R3 Structure Determination Manual"; Calabrese, J. C., Ed.; Nicolet XRD Corp.: Cupertino, CA, 1980.

(12) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 72–98.

(13) Stewart, R. F.; Davidson, R. F.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(14) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(15) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr. Sect. A* **1971**, *A27*, 368.

Table IV. Interatomic Distances (Å) and Esd's[a] for $Na_2[Ni(NH_2CH_2COO)_3]ClO_4 \cdot D_2O$

(a) Distances from Nickel Atom					
Ni-N(1)	2.091 (3)	2.091 ± 0.004[b]	Ni-O(1)	2.044 (2)	2.050 ± 0.009
Ni-N(2)	2.088 (2)		Ni-O(3)	2.047 (2)	
Ni-N(3)	2.095 (3)		Ni-O(5)	2.060 (2)	
(b) Distances within Glycinato Ligands					
N(1)-C(4)	1.450 (4)	1.446 ± 0.004	C(1)-C(4)	1.522 (5)	1.516 ± 0.005
N(2)-C(5)	1.442 (5)		C(2)-C(5)	1.514 (5)	
N(3)-C(6)	1.447 (5)		C(3)-C(6)	1.513 (6)	
O(1)-C(1)	1.267 (4)	1.264 ± 0.003	O(2)-C(1)	1.233 (3)	1.238 ± 0.009
O(3)-C(2)	1.262 (4)		O(4)-C(2)	1.248 (4)	
O(5)-C(3)	1.262 (4)		O(6)-C(3)	1.232 (4)	
(c) Distances within Perchlorate Anion					
Cl-O(7)	1.440 (4)	1.42 ± 0.02			
Cl-O(8)	1.432 (3)				
Cl-O(9)	1.388 (4)				
Cl-O(10)	1.424 (3)				

[a] Esd's (in parentheses) include the contribution of the cell constant errors and correlations between the parameters of a given atom. No account has been taken of possible correlations between the parameters of different atoms. [b] The standard deviations of the mean has been calculated from the formula $[\Sigma_i(\bar{d} - d_i)^2/n(n-1)]^{1/2}$.

syntheses revealed the locations of all remaining nonhydrogen atoms in the structure. A structure factor calculation based on these atomic sites and assuming an overall temperature factor of 2.5 Å^2 gave R_F = 24% for all 3226 significant structure factor amplitudes.

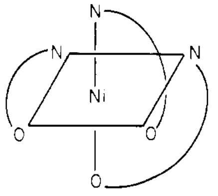
Refinement of the positional and individual isotropic thermal parameters of the nonhydrogen atoms by means of a block-diagonal least-squares procedure minimizing $\sum w(|F_o| - |F_c|)^2$ and using unit weights, w, gave convergence at R_F = 12.6%. At this point the coordinates of the 12 glycinato hydrogen atoms were calculated in idealized positions, and isotropic refinement of the nonhydrogen atoms was continued until convergence at R_F = 10.7% and R_{wF} = 11.7%. Individual ansiotropic thermal parameters were then assumed for all nonhydrogen atoms, and refinement was continued for six more cycles to yield R_F = 5.3% and R_{wF} = 8.0%. A difference map then revealed the locations of the two remaining hydrogen atoms on the water molecule. Several cycles of full-matrix least-squares refinement were then carried out in which the positions of all hydrogen atoms were varied along with positional and anisotropic thermal parameters on the nonhydrogen atoms. At convergence, the final values of R_F, R_{wF}, and GOF were 5.5%, 5.6%, and 1.436, respectively. The function $\sum w(|F_o| - |F_c|)^2$ showed no appreciable dependence upon either (sin θ)/λ or $|F_o|$. A final difference Fourier synthesis revealed no unusual features with the highest peak being 0.97 e/Å^3 at 0.6383, 0.7329, and 0.6004.

A table of observed and calculated structure factor amplitudes is available.[16] Positional parameters are collected in Table II; thermal parameters are listed in Table III.

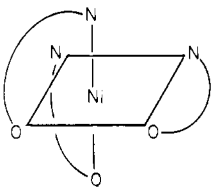
Results and Discussion

The unit cell of disodium *fac*-tris(glycinato)nickelate(II) perchlorate hydrate contains 8 $[Ni(Gly)_3]^-$ anions, 16 Na^+ cations, 8 ClO_4^- anions, and 8 water molecules of solvation. These species are arranged in layers perpendicular to the c axis. The sodium ions and water molecules are located at approximately z = 0.0, 0.5, and 1.0, while the perchlorate anions are located at approximately z = 0.25 and 0.75. The $[Ni(Gly)_3]^-$ anions are interspersed between the sodium and perchlorate layers in such a way that the nitrogen ends of the glycinato ligands are hydrogen bonded to perchlorate oxygen atoms and the oxygen ends of the glycinato ligands are directed toward the sodium cations.

The geometry of the *fac*-tris(glycinato)nickelate(II) anion is shown in Figure 1. The coordination about the central Ni(II) atom is approximately octahedral, with three oxygen atoms and three nitrogen atoms of the three bidentate glycinato ligands occupying the six coordination sites. The three glycinato ligands each form five-membered chelate rings at the nickel atom through their nitrogen atoms and one of their oxygen atoms. The arrangement of the ligands is such that the three nitrogen atoms are mutually cis, to yield a facial isomer which possesses an idealized C_3 geometry. The pseudothreefold axis is approximately parallel to the c axis of the unit cell, as illustrated by a comparison of the z coordinates for equivalent atoms (Table II). The complex exists in two enantiomeric forms (Λ and Δ), both of which are present in the unit cell by virtue of the crystallographic inversion center. The Λ isomers are arranged in two layers with 0.0 < z < 0.5, while the Δ isomers are arranged in two layers with 0.5 < z < 1.0.



Λ



Δ

The average Ni–O bond length of 2.050 (9) Å can be compared to analogous distances found in a variety of complexes, typically in the diaquobis(glycinato)nickel(II) complex, $[Ni(Gly)_2(H_2O)_2]$,[4] where they average 2.06 (1) Å, and in the isoelectronic tris(hydrazinecarboxylato-*N′*,*O*) nickelate(II) complex, $[Ni(Hyc)_3]^-$,[17] where they average 2.06 (1) Å. The average Ni–N bond length of 2.091 (4) Å is also similar to the average Ni–N bond distances of 2.08 (1) l and 2.11 (2) Å observed in $[Ni(Gly)_2(H_2O)_2]$[4] and $[Ni(Hyc)_3]^-$,[17] respectively. The observed Ni–N and Ni–O distances are within the range expected for outer orbital or high-spin octahedral nickel(II) complexes. The shortening of the Ni–O bonds relative to the Ni–N bonds is probably a result of the excess negative charge localized on the oxygen atoms. Similar trends in M–N vs. M–O distances have been observed for other transition metal amino acid complexes.[3]

The coordination geometry about the nickel atom is significantly distorted from octahedral symmetry with cis A–Ni–B angles ranging from 81.0 to 99.6° (Table V). One cause of this distortion from octahedral coordination is that the α-amino acid itself forms a five-membered chelate ring with an average O–Ni–N angle of 81.5 (6)°, which is conditioned by the "biting" distance of the chelating group with N···O = 2.70 (1) Å. Additional distortion is caused by the cis configuration about the nickel atom which results is nonbonded

---

(16) Supplementary material.

(17) Braibanti, A.; Manotti Lanfredi, A. M.; Tiripicchio, A. *Z. Kristallogr.* **1967**, *124*, 335.

Table V. Angles (Deg) and Esd's[a] for $Na_2[Ni(NH_2CH_2COO)_3]ClO_4{\cdot}D_2O$

(a) Angles around Nickel Atom					
N(1)-Ni-N(2)	98.2 (1)	98.4 ± 1.1[b]	O(1)-Ni-O(3)	88.6 (1)	89.1 ± 1.3
N(1)-Ni-N(3)	97.3 (1)		O(1)-Ni-O(5)	88.2 (1)	
N(2)-Ni-N(3)	99.6 (1)		O(3)-Ni-O(5)	90.6 (1)	
N(1)-Ni-O(1)	82.1 (1)	81.5 ± 0.5	N(1)-Ni-O(3)	90.9 (1)	91.0 ± 0.6
N(2)-Ni-O(3)	81.3 (1)		N(2)-Ni-O(5)	91.7 (1)	
N(3)-Ni-O(5)	81.0 (1)		N(3)-Ni-O(1)	90.4 (1)	
N(1)-Ni-O(5)	170.1 (1)	170.5 ± 0.9			
N(2)-Ni-O(1)	169.9 (1)				
N(3)-Ni-O(3)	171.5 (1)				
(b) Angles of Nickel Atom with Glycinato Ligands					
Ni-N(1)-C(4)	109.2 (2)	109.2 ± 0.4	Ni-O(1)-C(1)	115.8 (2)	116.0 ± 0.4
Ni-N(2)-C(5)	109.4 (2)		Ni-O(3)-C(2)	116.6 (2)	
Ni-N(3)-C(6)	108.9 (2)		Ni-O(5)-C(3)	115.7 (2)	
(c) Angles within Glycinato Ligands					
O(2)-C(1)-O(1)	125.0 (3)	124.6 ± 0.5	N(1)-C(4)-C(1)	114.2 (3)	114.4 ± 0.2
O(4)-C(2)-O(3)	124.7 (3)		N(2)-C(5)-C(2)	114.6 (3)	
O(6)-C(3)-O(5)	124.1 (3)		N(3)-C(6)-C(3)	114.3 (3)	
O(1)-C(1)-C(4)	117.8 (3)	117.3 ± 0.3	O(2)-C(1)-C(4)	117.2 (3)	118.1 ± 0.7
O(3)-C(2)-C(5)	116.9 (3)		O(4)-C(2)-C(5)	118.5 (3)	
O(5)-C(3)-C(6)	117.3 (3)		O(6)-C(3)-C(6)	118.6 (3)	
(d) Torsion Angles					
Ni-N(1)-C(4)-C(1)	9.3 (4)		N(1)-C(4)-C(1)-O(1)	−4.6 (5)	
Ni-N(2)-C(5)-C(2)	10.8 (4)		N(2)-C(5)-C(2)-O(3)	−5.1 (4)	
Ni-N(3)-C(6)-C(3)	14.7 (3)		N(3)-C(6)-C(3)-O(5)	−5.1 (4)	
(e) Angles within Perchlorate Anion					
O(7)-Cl-O(8)	107.4 (2)		O(8)-Cl-O(9)	111.7 (3)	
O(7)-Cl-O(9)	110.8 (3)		O(8)-Cl-O(10)	107.9 (2)	
O(7)-Cl-O(10)	106.3 (2)		O(9)-Cl-O(10)	112.4 (3)	
(f) Angle within Water Molecule					
H(13)-O(11)-H(14)	102 (5)				

[a] See footnote *a* in Table IV. [b] See footnote *b* in Table IV.

Table VI. Least-Squares Planes,[a,b] Deviation of Atoms from Those Planes, and Angles between Planes[c]

atom	dev, Å	atom	dev, Å
Plane IA: $-0.7055X + 0.3860Y + 0.5944Z = 2.6973$			
O(1)*	−0.0002 (21)	Ni	−0.1104 (4)
O(2)*	−0.0002 (24)	N(1)	0.0901 (29)
C(1)*	0.0007 (30)		
C(4)*	−0.0002 (44)		
Plane IB: $+0.0688X - 0.8015Y + 0.5941Z = 3.2190$			
O(3)*	−0.0009 (23)	Ni	−0.1398 (3)
O(4)*	−0.0010 (26)	N(2)	0.0991 (31)
C(2)*	0.0026 (30)		
C(5)*	−0.0007 (48)		
Plane IC: $+0.6345X + 0.5436Y + 0.5495Z = 8.3182$			
O(5)*	−0.0008 (21)	Ni	−0.2734 (4)
O(6)*	−0.0009 (36)	N(3)	0.1099 (30)
C(3)*	0.0023 (31)		
C(6)*	−0.0007 (46)		
Plane II: $+0.0355X + 0.0147Y + 0.993Z = 7.4893$			
N(1)*	0.000	Ni	−1.0163 (4)
N(2)*	0.000		
N(3)*	0.000		
Plane III: $+0.0251X + 0.0072Y + 0.9997Z = 9.6476$			
O(1)*	0.000	Ni	1.2012 (4)
O(3)*	0.000		
O(5)*	0.000		

[a] Equations to planes are expressed in orthonormal coordinates (X,Y,Z) which are related to the fractional coordinates (x,y,z) via the transformation

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & c\ \cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\ \sin\beta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

[b] Only atoms marked with an asterisk were included in calculation of the plane. [c] Important interplanar angles (deg): IA-IB, 90.3; IB-IC, 95.1; IC-IA, 93.8; II-III, 0.7; IA-II, 54.9; IB-II, 54.3; IC-II, 54.3; IC-II, 54.6; IA-III, 54.3; IB-III, 53.9; IC-III, 55.3.

O···O and N···N distances along the edges of the octahedron instead of N···O distances. The three coordinated oxygen atoms and the three coordinated nitrogen atoms lie in two nearly parallel planes (Table VI; planes II and III) with average N···N and O···O of 3.16 (3) and 2.88 (4) Å, respectively. The pseudoternary axis passes through these opposite faces of the distorted octahedron. The triangle formed by the three coordinated nitrogens has been rotated by approximately 52° with respect to the triangle formed by the coordinated oxygen atoms of the same ligands to give a trigonal antiprismatic coordination geometry about the nickel atom. Each of the glycinato chelate rings is tilted by approximately 36° with respect to the pseudothreefold axis.

The bond lengths in the chelate group are as expected. The average C–O(coordinated) distance of 1.264 (3) Å is signficantly longer than the average C–O(carbonyl) distance of 1.238 (9) Å, as it should be if the excess negative charge resides on the coordinated oxygen atom. A similar trend has been noted for numerous other transition-metal complexes with α-amino acids.[3] The average C–C distances of 1.516 (5) Å is similar to those found in the diaquobis(glycinato)nickel(II) complex (1.52 (1) Å),[4] the tris(glycinato)chromium(III) complex (1.517 (2) Å),[18] and the free α-glycine ligand (1.523 Å).[19] The average C–N distance of 1.446 (4) Å is slightly shorter than the corresponding distances of 1.47 (1), 1.479 (3), and 1.474 (5) Å observed in the $[Ni(Gly)_2(H_2O)_2]$[4] and $[Cr(Gly)_3]$[18] complexes and the free ligand,[19] respectively.

The five-membered ring is not planar. The deviations of the carbon and oxygen atoms are fairly small and do not appear to contradict the assumption of conjugation between these atoms. However, the nitrogen atoms and the nickel atom are, in general, significantly out of the plane. This means that the group C′–COO rotates around the N–C′ bond. This

---

(18) Byran, R. F.; Green, P. T.; Stokely, P. F.; Wilson, E. W., Jr. *Inorg. Chem.* **1971**, *10*, 1468.

(19) Marsh, R. E. *Acta Crystallogr. Sect. B* **1958**, *B11*, 654.

distortion can be approximately measured by the dihedral angle Ni–N–C′–C (12 ± 3°). Presumably, the lone pair of the nitrogen atom lies along the Ni–N line, and therefore the dihedral angle indicates, apart from a small distortion of the Ni–N bond, the rotation of the tetrahedral NH_2 group with respect to the C′–C line. The average O–C–C′–N torsional angle of −4.9 (3)° is also an indication of a systematic distoriton of the chelate rings involving a slight twist about the C′–N line. Similar distortions of the chelate rings have been observed in the isostructural $[Ni(Hyc)_3]^{-}$[17] and $[Cr(Gly)_3]$[18] complexes.

The complexes in this structure are held together by a network of hydrogen bonds.[16] All of the hydrogen atoms attached to the nitrogen atoms are involved as donors to oxygen atoms on the perchlorate anions with average N···O distances of 3.23 (6) Å and average H···O distances of 2.33 (5) Å. In addition, the hydrogen atoms of the water molecule form strong hydrogen bonds with O(2) and O(3) of adjacent $[Ni(Gly)_3{}^-$ anions with average O···O distances of 2.78 (5) Å and average H···O distances of 1.99 (6) Å. In all cases, the hydrogen atoms are slightly off the line joining the heavy atoms in accordance with the data quoted by Hamilton and Ibers and with the current view of bent hydrogen bonds.[20]

One of the sodium cations, Na(1), is in an approximately octahedral environment, being surrounded by six oxygen atoms of adjacent $[Ni(Gly)_3]^-$ units with Na···O distances ranging from 2.288 (3) to 2.828 (3) Å and cis angles ranging from 65.40 (7) to 103.14 (9)°.[16] The other sodium cation, Na(2), is in a much more irregular environment surrounded by six oxygen atoms from $[Ni(Gly)_3]^-$ anions and water molecules with Na···O distances ranging from 2.329 (3) to 2.945 (5) Å. In neither case are the sodium cations adjacent to oxygen atoms from the perchlorate anions.

The perchlorate anions exhibit the expected tetrahedral geometry with an average Cl–O distance of 1.42 (2) Å and with O–Cl–O angles ranging from 106.3 (2) to 112.4 (3)°. The anisotropic thermal parameters for the perchlorate oxygen atoms are rather large compared to the thermal factors for other atoms in this structure. The apparent highly anisotropic thermal behavior of these atoms, coupled with the large errors in thier thermal parameters, may be taken as an indication of a disorder in the positions of the perchlorate oxygen atoms.

Acknowledgment. We wish to acknowledge a departmental instrumentation grant from the National Science Foundation (CH-78091) which assisted in the purchase of the diffractometer and the structure determination and refinement system. We also thank Professor R. E. Tapscott, of this department, for helpful discussions.

Registry No. $Na_2[Ni(NH_2CH_2COO)_3]ClO_4{\cdot}D_2O$, 78919-05-8.

Supplementary Material Available: Listings of calculated and observed structure factor amplitudes, hydrogen bonds (Table VII), and Na···O contacts (Table VIII) (18 pages). Ordering information is given on any current masthead page.

---

(20) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968; p 64.

Contribution from the Department of Chemistry, Odense University,
DK-5230 Odense M, Denmark

Synthesis and Crystal Structure of Barium Tetrakis(μ-squarato-*O1,O2*)-diplatinate(II) Hexahydrate

O. SIMONSEN and H. TOFTLUND*

Received February 2, 1981

The new binuclear platinum(II) complex barium tetrakis(μ-squarato-*O1,O2*)-diplatinate(II) hexahydrate, $Ba_2[Pt_2(C_4O_4)_4]{\cdot}6H_2O$, has been prepared and characterized. The crystal and molecular structure has been determined by single-crystal X-ray analysis using three-dimensional diffractometer data. The compound crystallizes in the monoclinic space group $C2/m$, with two formula units in the unit cell. The lattice parameters are a = 17.8726 (8) Å, b = 8.1526 (5) Å, c = 8.7679 (5) Å, and β = 91.423 (5)°. A final residual value R = 0.073 was obtained by full-matrix minimization of $\sum(|F_o| - |F_c|)^2$ using 1881 independent observed reflections. The structure contains discrete (squarato-*O1,O2*)-bridged binuclear platinum(II) anions with a Pt–Pt distance of 3.061 Å. The crystal structure is stabilized by the water molecules, which are weakly coordinated to the barium ions and form hydrogen bonds between the squarate ions.

Introduction

Current interest in synthesis of new platinum salts of the Krogmann salt type prompts an investigation of the coordination chemistry of the squarate ion (the dianion of 3,4-dihydroxycyclobutenedione) toward platinum(II).

Chemically, the squarate ion is related to the oxalate ion, although it forms less stable metal complexes, normally with a 1:1 stoichiometry.

Reaction between tetraaquaplatinum(II) and squaric acid results in formation of bis(squarato)platinate(II) salts, which easily are partially oxidized.[1]

Besides these salts, some blue ill-defined species could be isolated. Krogmann has reported similar species of unknown structure formed as byproducts during the synthesis of the bis(oxalato)platinate(II) salts.[2] These species have several properties in common with the "platinum blues", and it is tempting to suggest a similar structure.

In the present paper we show that one of the platinum(II)–squarato complexes formed during the reaction between squaric acid and tetraaquaplatinum(II) has a squarato-bridged binuclear structure with some resemblance to the binuclear species isolated together with some of the "platinum blues".[3,4]

Experimental Section

Preparation. Squaric acid (Aldrich) (1 g, 8.77 mmol) was added to a tetraaquaplatinum(II) solution (100 mL, 0.02 M; 1 M $HClO_4$) prepared according to Elding.[5] The mixture was heated to 55 °C for 1 h, during which time the solution became dark. If platinum black is observed during this procedure, the heating must at once be interrupted and the solution must be filtered through a micropore filter before the preparation is continued. A saturated solution of sodium perchorate (5 mL) was added, and as the solution cooled to room temperature, a black precipitate of the partially oxidized bis(squarato)platinate(II) was formed. This product was filtered off after 2 h; yield 0.25 g, 25%. The mother liquor was dark blue, and from this another black precipitate was formed by slow evaporation during several days; yield 0.1 g.

---

(1) Toftlund, H. *J. Chem. Soc., Chem. Commun.* **1979**, 837.
(2) Krogmann, K.; Dodel, P. *Chem. Ber.* **1966**, *99*, 3408.
(3) Lock, C. J. L.; Peresie, H. J.; Rosenberg, B.; Turner, G. *J. Am. Chem. Soc.* **1978**, *100*, 3371.
(4) Lippert, B.; Neugebauer, D.; Schubert, U. *Inorg. Chim. Acta* **1980**, *46* L11.
(5) Elding, L. I. *Inorg. Chim. Acta* **1976**, *20*, 65.

0020-1669/81/1320-4044$01.25/0