SHORT STRUCTURAL PAPERS

Papers intended for publication under this heading must be in the format prescribed in Notes for Authors, Acta Cryst. (1973). B29, 154.

Acta Cryst. (1977). B33, 1251–1254

Lithium Bis(iminodiacetato)nickelate(II) Tetrahydrate and Cesium Bis(iminodiacetato)nickelate(II) Tetrahydrate

By N. J. Mammano,* D. H. Templeton† and Allan Zalkin

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California 94720, USA

(Received 9 August 1976; accepted 17 November 1976)

Abstract. $Li_2Ni[NH(CH_2COO)_2]_2.(H_2O)_4$, monoclinic, space group $P2_1/n$ (No. 14), $a = 9.785$ (5), $b = 5.312$ (3), $c = 15.770$ (7) Å, $\beta = 99.76$ (5)°, $Z = 2$, $d_m = 1.67$, $d_c = 1.672$ g cm^{-3}. $Cs_2Ni[NH(CH_2COO)_2]_2.(H_2O)_4$, monoclinic, space group $P2_1/c$ (No. 14), $a = 5.024$ (3), $b = 8.757$ (4), $c = 21.146$ (9) Å, $\beta = 96.51$ (5)°, $Z = 2$, $d_m = 2.31$, $d_c = 2.366$ g cm^{-3}. In each salt the two iminodiacetate (ida) ions which coordinate Ni function as tridentate ligands and are related by a center of inversion at the Ni atom, resulting in a *trans* configuration for the anion complex, $Ni(ida)_2^{2-}$. The coordination around Ni is in the shape of a distorted octahedron, and the two five-membered rings which result from the coordination of each ida molecule are not planar or equivalent by symmetry; this distortion is related to the bond strain and H atom repulsion within each ida molecule. The two salts are not isostructural.

Introduction. We studied these crystals to learn the isomeric identity, shape, and size of the $Ni(ida)_2^{2-}$ complex ion [ida $= NH(CH_2COO)_2^{2-}$] to aid in the interpretation of rates of ligand and water exchange for this and related complexes which are under investigation by Professor R. E. Connick and his co-workers in these laboratories. Single crystals of each compound were prepared by dissolving a stoichiometric mixture of $NiCl_2$ (1·75M), iminodiacetic acid(s) and the appropriate alkali-metal base in water, and slowly evaporating to dryness. X-ray measurements were made with a Picker FACS-I diffractometer with an oriented graphite monochromator. The crystal data and some experimental details are summarized in Table 1. Azimuthal scans indicated that no absorption correction would be necessary for the Li salt. Standard reflections, monitored after every 200th scan, showed that no correc-

tion for instrumental instability or crystal decay was required. Atomic scattering factors (Doyle & Turner, 1968) were used for Cs$^+$, Li$^+$, O, N, C, and H and were corrected for anomalous dispersion (Cromer & Liberman, 1970). Each structure was solved by three-dimensional Patterson and electron-density Fourier syntheses. Refinement was by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for H. An empirical correction for secondary extinction was determined by trial and error. The final unweighted residuals $(R_1 = \Sigma |\Delta F|/\Sigma |F_o|)$ were 0·031 and 0·024 for the 1796 and 2028 reflections used in the refinement of the Li and Cs salts, respectively, and 0·048 and 0·040 including the zero-weighted reflections. Corresponding weighted residuals $\{R_2 = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}\}$ were 0·034 and 0·030. Atomic coordinates and thermal

* On leave from Department of Chemistry, SUNY, Plattsburgh, NY 12901, USA.

† To whom correspondence should be addressed.

Table 1. *Summary of crystal data*

	$Li_2Ni(ida)_2.(H_2O)_4$	$Cs_2Ni(ida)_2.(H_2O)_4$
Formula weight	406·8	658·8
Crystal shape and size (mm)	needle: ~0·2 × 0·08	prism: ~0·2 × 0·15
Temperature (°C)	22–23	22–23
Radiation	Mo $K\alpha_1$ ($\lambda = 0.7093$ Å)	Mo $K\alpha_1$ ($\lambda = 0.7093$ Å)
Absorption correction	None	1·31 to 1·70; average correction 1·45
μ(cm^{-1})	11·9	47
Data collection method	θ–2θ(2° min^{-1})	θ–2θ(2° min^{-1})
2θ limits	3 to 50°	3 to 60°
Background counts, each end of scan (s)	10	10
Scan range (°)	1·2	1·2
Final number of variables	151	151
Total number of reflections	2378	2711
Unique data used	1796 ($I > 2\sigma$)	2028 ($I > 3\sigma$)
Extinction parameter	2·3 × 10^{-7}	2·65 × 10^{-6}

1251

Table 2. *Atomic parameters*

The form of the temperature factor is $\exp[-0.25(h^2a^{*2}B_{11} + 2hka^*b^*B_{12} + \cdots)]$ or $\exp(-B\lambda^{-2}\sin^2\theta)$, B_{ij} and B in Å^2. Positional parameters $\times 10^4$, for H $\times 10^3$.

(a) $Li_2Ni(ida)_2.(H_2O)_4$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	1.70(1)	1.41(1)	1.63(1)	−0.17(1)	−0.09(1)	0.03(1)
Li	9466(3)	2051(7)	3490(2)	2.3(1)	2.9(2)	2.7(1)	−0.2(1)	0.2(1)	0.1(1)
O(1)	1620(1)	−2465(3)	174(1)	2.27(6)	1.72(5)	3.29(7)	0.14(3)	−0.45(5)	−0.57(5)
O(2)	3781(2)	−2920(3)	815(1)	2.53(7)	2.82(7)	6.86(10)	0.86(6)	−1.15(6)	−0.88(7)
O(3)	−538(2)	−1275(3)	1136(1)	3.36(7)	2.55(6)	2.24(6)	−1.03(5)	0.54(5)	−0.04(5)
O(4)	−482(2)	−140(3)	2493(1)	6.43(10)	3.56(7)	2.72(6)	−1.37(8)	2.08(6)	−0.32(7)
O(5)	6331(2)	180(4)	1976(2)	3.41(8)	3.24(8)	7.44(13)	0.03(8)	0.25(8)	−2.11(9)
O(6)	7958(3)	771(5)	3997(2)	5.30(12)	4.23(10)	5.81(12)	0.96(9)	3.20(10)	1.96(9)
N	1351(2)	2229(3)	844(1)	2.04(6)	1.31(6)	1.91(6)	−0.13(5)	0.12(5)	0.13(5)
C(1)	2710(2)	−1647(4)	636(1)	2.12(7)	1.69(7)	2.59(8)	−0.01(6)	0.11(6)	−0.01(6)
C(2)	2727(2)	1046(4)	957(2)	1.93(7)	2.07(8)	3.06(9)	−0.29(7)	−0.21(7)	−0.33(7)
C(3)	751(2)	2405(4)	1638(1)	3.38(9)	2.17(8)	2.28(8)	−0.54(7)	0.74(7)	−0.54(7)
C(4)	−148(2)	147(4)	1769(1)	2.83(7)	2.12(7)	2.35(7)	0.02(8)	0.63(6)	0.21(8)

	x	y	z	B		x	y	z	B
H(1)	141(2)	369(5)	65(2)	2.6(5)	H(6)	708(5)	21(8)	205(3)	8.5(14)
H(2)	336(2)	197(5)	64(2)	3.4(2)	H(7)	608(3)	138(6)	215(2)	4.3(8)
H(3)	319(3)	112(6)	150(2)	4.2(6)	H(8)	818(4)	−13(7)	426(3)	6.2(12)
H(4)	150(2)	262(5)	216(2)	3.2(5)	H(9)	726(5)	143(10)	399(10)	10.0(15)
H(5)	15(3)	391(6)	161(2)	4.5(6)					

(b) $Cs_2Ni(ida)_2.(H_2O)_4$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	5000	5000	5000	1.49(2)	1.30(1)	2.03(2)	0.07(1)	0.30(1)	0.14
Cs	9670.4(4)	9396.6(2)	7019.1(1)	3.55(1)	2.84(1)	3.15(1)	0.11(1)	−0.12(1)	−0.33(1)
O(1)	2592(4)	5705(2)	4205(1)	2.01(7)	3.15(9)	2.90(9)	−0.44(5)	−0.33(6)	0.88(7)
O(2)	2580(5)	7092(3)	3331(1)	3.2(1)	5.0(1)	2.8(1)	0.37(9)	−0.55(8)	1.21(9)
O(3)	3411(4)	6667(2)	5519(1)	2.60(8)	2.17(7)	3.7(1)	−0.30(6)	1.33(7)	−0.73(7)
O(4)	4452(5)	8894(3)	5991(1)	4.3(1)	2.51(8)	3.6(1)	0.08(8)	1.03(9)	−0.98(8)
O(5)	1154(6)	6047(3)	6611(1)	4.2(1)	4.5(1)	2.7(1)	−1.7(1)	0.92(9)	−0.95(9)
O(6)	5850(6)	6692(4)	7495(2)	3.6(1)	6.5(2)	3.5(1)	0.5(1)	−0.1(1)	−0.8(1)
N	7374(4)	6815(2)	4750(1)	1.45(8)	1.59(7)	2.32(9)	0.09(6)	0.20(7)	0.14(6)
C(1)	3647(5)	6647(3)	3859(1)	2.1(1)	2.3(1)	2.4(1)	0.27(8)	0.01(8)	0.18(8)
C(2)	6384(6)	7286(3)	4100(1)	2.3(1)	2.2(1)	2.2(1)	−0.24(8)	0.28(8)	0.31(8)
C(3)	7223(6)	8015(3)	5232(1)	2.6(1)	2.1(1)	2.5(1)	−0.56(8)	0.22(9)	−0.12(9)
C(4)	4846(5)	7870(3)	5611(1)	2.3(1)	1.92(9)	2.4(1)	0.45(8)	0.12(8)	−0.01(8)

	x	y	z	B		x	y	z	B
H(1)	889(9)	658(5)	477(2)	3.6(9)	H(6)	172(9)	630(5)	630(2)	3.9(9)
H(2)	762(7)	691(4)	383(2)	2.7(7)	H(7)	9(11)	539(6)	651(3)	5.5(12)
H(3)	634(7)	836(4)	407(2)	2.5(7)	H(8)	491(9)	640(6)	723(2)	4.0(10)
H(4)	727(8)	896(5)	506(2)	3.6(8)	H(9)	481(9)	709(5)	775(2)	4.1(10)
H(5)	883(8)	788(4)	554(2)	4.0(9)					

parameters are listed in Table 2 and selected bond distances and angles in Table 3.*

Discussion. The two compounds are not isostructural. In each salt the cation is in a general position. The Li+ ion is surrounded by four O atoms at the corners of a

not very regular tetrahedron, two belonging to water molecules and two from the acetate groups of the ida molecule; O—Li—O angles range from 100 to 119°. The Cs+ ion is surrounded by eight O atoms, four from water molecules and four from acetate groups. These neighbors are at the corners of a polyhedron which is closer to a square antiprism than to any other simple shape, but O—Cs—O angles, which would be equal for a regular antiprism, range from 61 to 103°. The structure determined here for $Li_2Ni(ida)_2.(H_2O)_4$ is in agreement with preliminary (unrefined) results reported (Kramarenko, Polynova, Poray-Koshits, Chayli &

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32308 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Interatomic distances* (Å) *and angles* (°)

(a) Ni(ida)$_2^{2-}$

	Li salt	Cs salt
Ni—N	2·079 (2)	2·091 (2)
Ni—O(1)	2·038 (2)	2·052 (2)
Ni—O(3)	2·065 (2)	2·042 (2)
C(1)—C(2)	1·517 (3)	1·518 (4)
C(1)—O(1)	1·263 (2)	1·259 (4)
C(1)—O(2)	1·238 (2)	1·244 (4)
C(4)—C(3)	1·522 (3)	1·517 (4)
C(4)—O(3)	1·259 (3)	1·279 (3)
C(4)—O(4)	1·249 (2)	1·235 (3)
C(2)—N	1·469 (3)	1·467 (4)
C(3)—N	1·473 (3)	1·472 (4)
C(2)—N—C(3)	114·4 (2)	114·2 (2)
Ni—N—C(2)	107·7 (1)	107·9 (2)
Ni—N—C(3)	106·2 (1)	107·0 (2)
N—C(3)—C(4)	112·9 (2)	114·3 (2)
N—C(2)—C(1)	113·9 (2)	114·1 (2)
C(2)—C(1)—O(1)	118·5 (2)	118·1 (2)
C(2)—C(1)—O(2)	118·5 (2)	117·8 (3)
O(1)—C(1)—O(2)	122·9 (2)	124·0 (3)
C(3)—C(4)—O(3)	118·0 (2)	117·0 (2)
C(3)—C(4)—O(4)	117·9 (2)	118·5 (2)
O(3)—C(4)—O(4)	124·1 (2)	124·6 (3)
Ni—O(1)—C(1)	114·7 (1)	115·2 (2)
Ni—O(3)—C(4)	113·8 (1)	115·0 (2)
N—Ni—O(1)	83·4 (1)	82·2 (1)
N—Ni—O(3)	81·9 (1)	82·0 (1)
O(1)—Ni—O(3)	88·8 (1)	89·7 (1)
O(1)—Ni—C(3)	95·2 (1)	92·6 (1)
O(1)—Ni—C(4)	93·1 (1)	93·6 (1)
O(3)—Ni—C(1)	87·3 (1)	91·3 (1)
O(3)—Ni—C(2)	87·6 (1)	89·8 (1)

(b) Li and Cs coordination

Li—O(2^i)	1·873 (4)	Cs—O(4^{ii})	3·447 (3)	
Li—O(4^{ii})	1·963 (4)	Cs—O(4)	3·241 (3)	
Li—O(5^i)	1·928 (4)	Cs—O(5^{vi})	3·305 (3)	
Li—O(6)	1·918 (4)	Cs—O(5^{ii})	3·170 (3)	
Li—O(ave.)	1·920	Cs—O(6^{vii})	3·104 (3)	
Cs—O(2^{iv})	3·331 (3)	Cs—O(6)	3·278 (4)	
Cs—O(^{v})	3·258 (3)	Cs—O(ave.)	3·267	

(c) Hydrogen bonding, Li salt

O(5)—H(6)	0·72 (5)	O(5)—H(6)—O(4^{ii})	170 (4)
O(5)—H(7)	0·75 (3)	O(5)—H(7)—O(4^{iii})	174 (2)
O(5)—O(4^{iii})	3·091 (4)	O(4^{ii})—O(5)—O(4^{iii})	107·9 (1)
O(5)—O(4^{iii})	2·794 (3)	H(6)—O(5)—H(7)	108 (4)
O(6)—H(8)	0·65 (4)	O(6)—H(9)—O(3)	170 (4)
O(6)—H(9)	0·76 (5)	H(8)—O(6)—H(9)	124 (5)
O(6)—O(3^{iii})	2·819 (3)		

(d) Hydrogen bonding, Cs salt

O(5)—H(6)	0·78 (5)	O(5)—H(6)—O(3)	172 (3)
O(5)—H(7)	0·80 (5)	O(5)—H(7)—O(1^{viii})	149 (4)
O(5)—O(3)	2·740 (4)	H(6)—O(5)—H(7)	106 (5)
O(5)—O(1^{viii})	2·853 (4)	O(3)—O(5)—O(1^{viii})	84·5 (1)
O(6)—H(8)	0·74 (5)	O(6)—H(8)—O(5)	160 (4)
O(6)—H(9)	0·87 (5)	O(6)—H(9)—O(2^{ix})	178 (3)
O(6)—O(5)	2·894 (5)	H(8)—O(6)—H(9)	104 (4)
O(6)—O(2^{ix})	2·760 (4)	O(5)—O(6)—O(2^{ix})	89·3 (1)

Symmetry code

(i)	$\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$		(vi)	$1 - x, \frac{1}{2} + y, \frac{3}{2} - z$
(ii)	$1 + x, y, z$		(vii)	$2 - x, \frac{1}{2} + y, \frac{3}{2} - z$
(iii)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$		(viii)	$-x, 1 - y, 1 - z$
(iv)	$1 - x, 2 - y, 1 - z$		(ix)	$x, \frac{3}{2} - y, \frac{1}{2} + z$
(v)	$1 + x, \frac{3}{2} - y, \frac{1}{2} + z$			

Mitrofanova, 1974), but with a different choice of unit-cell setting.

In each salt, the complex anion Ni(ida)$_2^{2-}$ has the same *trans* configuration (Fig. 1). Ni is at a special position, so that the two halves of the complex are related by a center of symmetry at Ni. The N—Ni—N axis is not perpendicular to the plane of O atoms but is inclined toward the direction in which each ida ligand chelates; this distortion is about the same in each salt (N—Ni—O bond angles, Table 3). In the equatorial plane all O(1)—Ni—O(3) bond angles are close to 90°. The two five-membered rings, Ni—N—C—C—O, resulting from the tridentate chelation by each ida molecule are not symmetrically equivalent and are puckered. This distortion, which differs slightly for each salt, is small, amounting to displacements of the ring C atoms from the Ni—N—O plane of 0·1 to 0·6 Å. A model of the complex, constructed so as to constrain Ni into octahedral coordination (N—Ni—O bond angles of 90°) and the N, O and ring C atoms into tetrahedral coordination (bond angles of 109·5°), revealed a substantial degree of bond strain, making it difficult to fasten all the bonds simultaneously. This bond strain within each five-membered ring leads to a constriction of the N—Ni—O bond angles to ~ 82°, and a deviation of the bond angles about the N, O and ring C atoms from the tetrahedral value (Table 3). A further distortion involves torsion of the Ni—N bond and puts C(1) and C(2) closer to O(3) than C(4) and C(3) are to O(1). The most obvious purpose of this twisting of the rings is to increase the distance between H(3) and H(4), which, even so, is 2·24 (4) and 2·16 (5) Å in the Li and Cs salts. The Ni—N and Ni—O bond distances listed in Table 3 are well within the range established for these bonds. For example, in the tridentate complex,
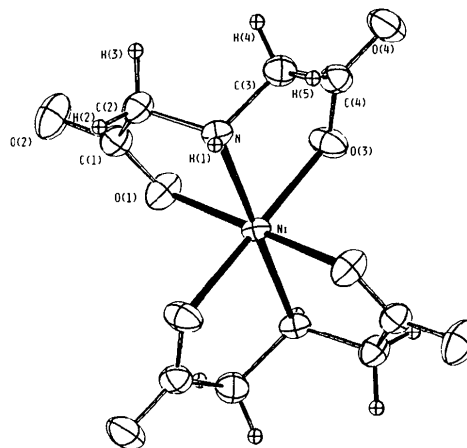

Fig. 1. The bis(iminodiacetato)nickelate(II) complex in the Cs salt, drawn with Johnson's *ORTEP*. The same atomic numbering is used for the Li salt.

potassium bis(triacetonitrito)nickel(II) octahydrate, $K_4Ni[N(CH_2COO)_3]_2.(H_2O)_8$, the Ni—N and Ni—O bond distances are 2·12 and 2·06 Å respectively (Fomenko, Polynova, Poray-Koshits & Mitrofanova, 1972). The structure of the bis|2,2′-iminobis(acetamidoxime)]nickel(II) cation in a chloride hydrate (Cullen & Lingafelter, 1970) is very similar in shape and dimensions to our Ni complex, with allowance for the slightly longer distance where Ni—N takes the place of Ni—O, and disregarding a few extra peripheral atoms. Angles in the chelate rings and at Ni agree within 2° on average with the values reported here for corresponding angles.

In the Cs salt, all of the H atoms of water molecules are involved in hydrogen bonds to other O atoms; relevant distances and angles are listed in Table 3. In the Li salt, H(7) and H(9) are well situated for hydrogen bonds, while H(6) may weakly hydrogen-bond (Table 3). In this salt, H(8) has no neighbor suitable for hydrogen bonding.

References

CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.

CULLEN, D. L. & LINGAFELTER, E. C. (1970). Inorg. Chem. 9, 1865–1877.

DOYLE, P. A. & TURNER, P. S. (1968). Acta Cryst. A24, 390–397.

FOMENKO, V. V., POLYNOVA, T. N., PORAY-KOSHITS, M. A. & MITROFANOVA, N. D. (1972). Zh. Strukt. Khim. 13, 343–344.

KRAMARENKO, F. G., POLYNOVA, T. N., PORAY-KOSHITS, M. A., CHAYLI, V. P. & MITROFANOVA, N. D. (1974). Zh. Strukt. Khim. 15, 161.

9-Methyl-9-(3-dimethylaminopropyl)-9,10-dihydrosilaanthracene Hydrochloride

By Eugene R. Corey,* Joyce Y. Corey and William F. Paton

Department of Chemistry, University of Missouri–St Louis, St Louis, Missouri 63121, USA

and Milton D. Glick

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

Abstract. $C_{19}H_{26}ClNSi$, $M_r = 331·96$; monoclinic, $P2_1/c$, $a = 17·207$ (4), $b = 6·915$ (2), $c = 17·066$ (4) Å, $\beta = 104·18$ (2)°; $Z = 4$, $D_m = 1·13$ (1), $D_c = 1·12$ g cm⁻³, $U = 1968·8$ (9) Å³; μ(Mo $K\alpha$) = 2·54 cm⁻¹. A folded conformation is adopted with a dihedral angle between benzo group planes of 132·1° and an extended dimethylaminopropyl side chain in the pseudoaxial position on the Si hetero-atom.

Introduction. Crystals of the title compound were prepared by J. Y. Corey. The product was purified and recrystallized from xylene–chloroform mixtures.† A crystal 0·3 × 0·3 × 0·2 mm was mounted on a Syntex

---

* To whom correspondence should be addressed.

† Details of the synthetic procedures will be published at a later date.

$P2_1$ diffractometer and data were collected to $2\theta = 52°$ with Mo $K\alpha$ ($\lambda = 0·71069$ Å) radiation (graphite monochromator) and the θ–2θ scan technique at 2° min⁻¹. Backgrounds were measured at each end of the scan [2θ scan range: 2θ(Mo $K\alpha_1$) − 1·0° to 2θ(Mo $K\alpha_2$) + 1·0°] for a total time equal to one-half the scan time. Systematic absences were $h0l$, l odd; $0k0$, k odd, uniquely determining the space group $P2_1/c$. Fifteen reflections with 2θ between 20 and 28° were centered with a programmed centering routine; cell parameters were obtained by least-squares refinement of these angles. During data collection, the intensities of three standard reflections were measured every 97 reflections with no significant variation in intensity observed. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those described previously (Schmonsees, 1974; Mivake, Togawa & Hosoya, 1964). Standard