

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MISSOURI, COLUMBIA, MISSOURI 65201

The Crystal Structure of Bis(2-amino-2-methyl-3-butanone oximato)nickel(II) Chloride Monohydrate

By E. O. SCHLEMPER

Received December 4, 1967

The crystal structure of bis(2-amino-2-methyl-3-butanone oximato)nickel(II) chloride monohydrate, $C_{10}H_{26}N_4O_2NiCl \cdot H_2O$, has been determined from three-dimensional X-ray diffraction data. Unit cell dimensions are $a = 12.74 \pm 0.02 \text{ \AA}$, $b = 10.79 \pm 0.02 \text{ \AA}$, $c = 11.81 \pm 0.02 \text{ \AA}$, and $\beta = 92.5 \pm 0.2^\circ$. The space group is $P2_1/c$. The density by flotation is 1.39 g/cm^3 . Four formula units in the unit cell gives a calculated density of 1.40 g/cm^3 . By visual estimation of film data, the intensities of 1335 independent reflections were obtained. The structure was solved by three-dimensional Patterson and Fourier methods and refined by full-matrix least squares to a conventional R factor of 7.1%. The arrangement of nitrogen atoms about the nickel atom is square-planar with the bond distances: Ni-N (oxime), 1.85 and 1.86 \AA ; Ni-N (amine), 1.91 and 1.91 \AA . The intramolecular O...O distance involved in the hydrogen bond is 2.38 \AA . Intermolecular hydrogen bonding involving the chloride ion, the water molecule, and the amine nitrogens of the cation stabilizes the crystal structure.

Introduction

The presence of short intramolecular hydrogen bonds in bis(dimethylglyoximato)nickel(II) was demonstrated by Godycki and Rundle.¹ Since that time the structures of other metal complexes of glyoxime and its derivatives have been established. The following features have been observed: (1) in the nickel complexes^{1,2} short intramolecular oxygen-oxygen distances (2.40–2.45 \AA) were always found; (2) in the palladium dimethylglyoxime complex^{1,3} the oxygen-oxygen distances (2.59–2.62 \AA) proved to be considerably greater while in the platinum dimethylglyoxime complex⁴ the oxygen-oxygen distance (3.03 \AA) was still greater; and (3) in the copper dimethylglyoxime complex⁵ two different oxygen-oxygen distances (2.53 and 2.70 \AA) were observed. The oxygen-oxygen distances in the nickel complexes are short enough to suggest symmetrical hydrogen bonds, but it is unlikely that those for the palladium and platinum complexes are symmetrical. None of these compounds has been conclusively shown to have symmetrical hydrogen bonds. Neutron diffraction would provide the most powerful method of approach, but efforts have been hampered by the difficulty in growing crystals large enough for the experiment.

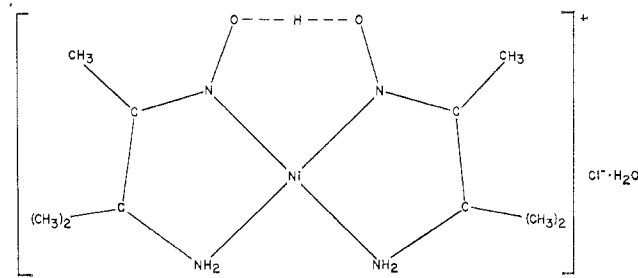
Amino oxime-metal complexes have been known for some time.⁶ Potentially, these complexes have one short intramolecular hydrogen bond rather than two. The presence of this hydrogen bond has been inferred from infrared⁶ and nmr data.⁷ One can grow rather large single crystals of these cationic complexes for neutron diffraction studies. With only one intramolecular hydrogen bond, there is a possibility that the bond

is symmetric for complexes of a number of different metal ions. The author plans to examine the structures of a series of these complexes by X-ray and neutron diffraction techniques. The present paper gives the results for bis(2-amino-2-methyl-3-butanone oximato)nickel(II) chloride monohydrate.

Experimental Section

Crystal Preparation.—The crystals used in this work were kindly supplied by Murmann and were prepared by the reported method.⁶

X-Ray Data.—Bis(2-amino-2-methyl-3-butanone oximato)nickel(II) chloride monohydrate crystallizes in the monoclinic



crystal system with four molecules in a unit cell of dimensions: $a = 12.74 \pm 0.02$, $b = 10.79 \pm 0.02$, $c = 11.81 \pm 0.02 \text{ \AA}$, and $\beta = 92.5 \pm 0.2^\circ$. The reported errors represent the average deviations in the observed cell constants as measured from precession photographs from a camera calibrated with NaCl. A crude flotation measurement of the density in carbon tetrachloride-benzene solution gave $1.39 \pm 0.01 \text{ g/cm}^3$. A calculated density of $1.407 \pm 0.004 \text{ g/cm}^3$ is obtained, assuming four formula units per unit cell. The systematic extinctions were for $h0l$, l odd, and for $0k0$, k odd, indicating that the space group is $P2_1/c$.

A crystal approximately $0.20 \times 0.20 \times 0.30 \text{ mm}$, mounted with the long dimension as the rotation axis, was chosen for intensity measurements. Using a Zr filter and brass interleaving sheets, multiple-film Mo $K\alpha$ Weissenberg photographs were taken of the $0kl-11kl$ zones, and multiple exposures were taken of the $h0l$, $hk1$, $h0l$, and $h1l$ zones by the precession method. The relative intensities were estimated by visual comparison with a series of timed exposures of a selected reflection. There were 1335 independent reflections of measurable intensity. The usual Lorentz and polarization corrections were made. Absorption corrections were not made ($\mu = 14.2 \text{ cm}^{-1}$). A rough

(1) (a) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953); (b) D. E. Williams, G. Wohlaer, and R. E. Rundle, *J. Am. Chem. Soc.*, **81**, 755 (1959).

(2) M. Calleri, G. Ferraris, and D. Viterbo, *Acta Cryst.*, **22**, 468 (1967); R. K. Murmann and E. O. Schlemper, *ibid.*, **23**, 667 (1967).

(3) C. Panattoni, E. Frasson, and R. Zannetti, *Gazz. Chim. Ital.*, **89**, 2132 (1959).

(4) E. Frasson, C. Panattoni, and R. Zannetti, *Acta Cryst.*, **12**, 1027 (1959).

(5) E. Frasson, R. Bardi, and S. Bezzi, *ibid.*, **12**, 201 (1959).

(6) R. K. Murmann, *J. Am. Chem. Soc.*, **79**, 521 (1957).

(7) R. K. Murmann, private communication.

TABLE I
OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 10$)

| OBSERVED | | | | | | | | | | CALCULATED | | | | | | | | | | STRUCTURE FACTORS | | | | | | | | | | | | | | | | | | | | | | | |
|----------|---|------|------|---|---|-----|-----|---|---|------------|-----|---|---|-----|-----|---|----|-----|-----|-------------------|----|-----|-----|---|----|-----|-----|---|----|-----|-----|---|---|-----|-----|---|---|-----|-----|---|---|-----|-----|
| K | L | FO | FC | K | L | FO | FC | K | L | FO | FC | K | L | FO | FC | K | L | FO | FC | K | L | FO | FC | K | L | FO | FC | K | L | FO | FC | | | | | | | | | | | | |
| 0 | 0 | 1486 | 1505 | 5 | 7 | 417 | 416 | 3 | 4 | 221 | 396 | 1 | 5 | 861 | 875 | 0 | 17 | 160 | 175 | 0 | 10 | 840 | 828 | 7 | -5 | 485 | 497 | 7 | -1 | 249 | 246 | 0 | 4 | 248 | 297 | 7 | 5 | 269 | 225 | 1 | 0 | 222 | 183 |
| 0 | 0 | 1486 | 1505 | 5 | 7 | 417 | 416 | 3 | 4 | 221 | 396 | 1 | 5 | 861 | 875 | 0 | 17 | 160 | 175 | 0 | 10 | 840 | 828 | 7 | -5 | 485 | 497 | 7 | -1 | 249 | 246 | 0 | 4 | 248 | 297 | 7 | 5 | 269 | 225 | 1 | 0 | 222 | 183 |
| 0 | 0 | 1486 | 1505 | 5 | 7 | 417 | 416 | 3 | 4 | 221 | 396 | 1 | 5 | 861 | 875 | 0 | 17 | 160 | 175 | 0 | 10 | 840 | 828 | 7 | -5 | 485 | 497 | 7 | -1 | 249 | 246 | 0 | 4 | 248 | 297 | 7 | 5 | 269 | 225 | 1 | 0 | 222 | 183 |

estimate⁸ of the absorption factors for a given Weissberg layer indicated a range of less than 10%. The data were placed on a common scale using the interlayer scaling program of Hamilton, Rollett, and Sparks.

Determination of the Structure.—The calculations described above and below were made on the IBM 7040 computer of the Computer Research Center of the University of Missouri. The programs used in this work were A. Zalkin's *FORDAP* Program, W. R. Busing and H. A. Levy's *ORFLS* least-squares and *ORFFE* error-function programs, and data-handling programs of W. C. Hamilton and J. A. Ibers.

A three-dimensional Patterson synthesis was prepared. The Ni-Ni, Ni-Cl, and Cl-Cl vectors could all be located, and positions for the nickel and chlorine atoms were obtained. After least-squares refinement of the nickel and chlorine positions, the agreement factors were $R = \Sigma(|F_o|^2 - |kF_c|^2) / \Sigma|F_o|^2 = 0.64$, and $r = [\Sigma w(|F_o|^2 - |kF_c|^2)^2 / \Sigma w|F_o|^2]^{1/2} = 0.75$. For $(0.145F_o)^2 \leq 36$, $w = (1/7.2)^2$, and for $(0.145F_o)^2 > 36$, $w =$

$[1/0.20(0.148F_o)^2]^2$. In this and subsequent calculations, scattering factors^{9a} for neutral atoms were used. Using the tabulated values^{9b} of f' and f'' for Ni and Cl, the effects of anomalous dispersion were included in F_o .^{9c}

A three-dimensional Fourier synthesis was prepared with the phases from the observed structure factors and the magnitudes from the carbon, nitrogen, and oxygen atoms were located, being the highest net peaks present. After four cycles of full-matrix isotropic refinement, the agreement factors were $R = 0.143$ and $r = 0.200$. This and all subsequent least-squares cycles minimized the numerator of r . Two cycles of refinement with the nickel and chlorine atoms anisotropic converged with R equal to 0.142 and r equal to 0.197. At this stage the weighting scheme was modified to make the mean value of $|\Delta F|/\sigma$ nearly independent of F_o .¹⁰ For subsequent cycles $w = 1/\sigma^2$ where $\sigma =$

(9) "International Tables for X-ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962: (a) p. 202; (b) 216; (c) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1962).

(8) "International Tables for X-ray Crystallography," Vol. 2, The Kynoch Press, Birmingham, England, 1958, pp 291-312.

(10) R. A. Lalancette, M. Cefola, W. C. Hamilton, and S. J. LaPlaca, *Inorg. Chem.*, **6**, 2127 (1967).

TABLE II
 ATOMIC POSITIONAL AND THERMAL PARAMETERS^a

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> |
|------------------|--------------|--------------|--------------|----------|
| Ni | -0.2371 (1) | -0.0141 (1) | 0.0534 (1) | ... |
| Cl | 0.4726 (2) | -0.0342 (3) | 0.2057 (3) | ... |
| O(1) | -0.1020 (7) | -0.1485 (9) | 0.2010 (8) | 4.2 (2) |
| N(1) | -0.1867 (7) | -0.1548 (9) | 0.1277 (9) | 2.7 (2) |
| O(2) | -0.0460 (7) | 0.0575 (8) | 0.1649 (8) | 4.1 (2) |
| N(2) | -0.1228 (8) | 0.0884 (9) | 0.0871 (8) | 2.9 (2) |
| N(3) | -0.3561 (8) | -0.1163 (9) | 0.0178 (8) | 2.8 (2) |
| N(4) | -0.2909 (7) | 0.1297 (9) | -0.0228 (8) | 2.8 (2) |
| C(1) | -0.2345 (9) | -0.2604 (11) | 0.1092 (11) | 2.7 (2) |
| C(2) | -0.1141 (9) | 0.1902 (12) | 0.0313 (11) | 2.9 (2) |
| C(3) | -0.3259 (9) | -0.2531 (11) | 0.0246 (10) | 2.5 (2) |
| C(4) | -0.2021 (10) | 0.2137 (12) | -0.0539 (11) | 3.0 (2) |
| C(5) | -0.1937 (11) | -0.3792 (14) | 0.1620 (12) | 4.0 (3) |
| C(6) | -0.0213 (11) | 0.2755 (14) | 0.0477 (13) | 4.4 (3) |
| C(7) | -0.4191 (11) | -0.3302 (13) | 0.0594 (12) | 3.9 (3) |
| C(8) | -0.2905 (11) | -0.2961 (13) | -0.0938 (13) | 4.2 (3) |
| C(9) | -0.2385 (10) | 0.3480 (14) | -0.0571 (12) | 4.1 (3) |
| C(10) | -0.1628 (1) | 0.1732 (14) | -0.1729 (13) | 4.3 (3) |
| H ₂ O | -0.4060 (8) | 0.2175 (10) | 0.1700 (9) | 5.4 (2) |

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|----|--------------|--------------|--------------|--------------|--------------|--------------|
| Ni | 0.0032 (1) | 0.0054 (1) | 0.0048 (1) | 0.0006 (1) | -0.0002 (1) | 0.0002 (1) |
| Cl | 0.0054 (2) | 0.0078 (4) | 0.0065 (3) | 0.0001 (2) | 0.0004 (2) | -0.0001 (3) |

^a Standard deviations are in parentheses. The anisotropic temperature factors for the Ni and Cl atoms are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

-0.00013(0.186 F_o)⁴ + 0.32(0.186 F_o)² for (0.186 F_o)² ≤ 37.6; $\sigma = -0.00010(0.186F_o)^4 + 0.30(0.186F_o)^2$ for 37.6 < (0.186 F_o)² ≤ 56.5; $\sigma = 0.12(0.186F_o)^2$ for 56.5 < (0.186 F_o)² ≤ 225.9; and $\sigma = 0.14(0.186F_o)^2$ for (0.186 F_o)² > 225.9. Two more cycles of refinement with nickel and chlorine anisotropic gave convergence with $R = 0.141$ and $r = 0.190$. The estimated error in an observation of unit weight was 0.95. The maximum shift in any positional parameter at this stage was less than one-tenth the estimated standard deviation of that parameter. The conventional agreement factor $R^* = \Sigma(|F_o| - |kF_c|)/\Sigma|F_o|$ was 0.081.

A Fourier synthesis using the observed structure factors with phases from the last calculated structure factors showed the weakest carbon peaks with a density of 5.5 e⁻/Å³. The largest peak on the corresponding difference Fourier was one of density 0.8 e⁻/Å³, but this peak was almost exactly at the nickel atom position. Of the next 30 peaks (densities from 0.4 to 0.7 e⁻/Å³), 25 were in chemically reasonable positions for the 25 hydrogen atoms. Including these 25 hydrogens ($B = 5.5$) in a structure factor calculation gave $R = 0.12$ and $r = 0.169$. The conventional agreement factor R^* was 0.071. The observed and calculated structure factors ($\times 10$) from this model are included in Table I. The positional and thermal parameters are given in Tables II and III.

Attempts to refine the hydrogen atom positions were unsuccessful; some parameters converged but others did not. The parameters reported in Table III are based upon the difference Fourier synthesis.

Discussion

Nature of the Structure.—The nickel atom in the complex cation (Figure 1) is coordinated with square-planar geometry to the two amine nitrogens and the two oxime nitrogens. The closest contact of water or chlorine to the nickel involves a water molecule at 3.61 Å. This water is not in one of the octahedral positions but rather is 2.92 Å from N(4) to which it is hydrogen bonded. The nickel and four nitrogens define a weighted least-squares plane which in the monoclinic coordinate system has the equation: $5.83x - 3.22y$

 TABLE III
 HYDROGEN ATOM POSITIONS

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | Atom | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|----------|----------|----------|-------|----------|----------|----------|
| H(1) | -0.35 | -0.19 | 0.34 | H(14) | -0.26 | 0.13 | 0.51 |
| H(2) | -0.25 | -0.25 | 0.40 | H(15) | -0.14 | 0.14 | 0.45 |
| H(3) | -0.26 | -0.12 | 0.41 | H(16) | 0.13 | 0.15 | 0.30 |
| H(4) | 0.01 | 0.22 | 0.06 | H(17) | 0.25 | 0.10 | 0.30 |
| H(5) | -0.01 | 0.21 | 0.48 | H(18) | 0.18 | 0.09 | 0.38 |
| H(6) | 0.05 | -0.17 | 0.43 | H(19) | -0.40 | -0.09 | 0.07 |
| H(7) | 0.48 | 0.18 | 0.49 | H(20) | 0.37 | 0.11 | 0.04 |
| H(8) | 0.37 | 0.07 | 0.44 | H(21) | 0.33 | -0.09 | 0.07 |
| H(9) | 0.45 | 0.20 | 0.38 | H(22) | -0.33 | 0.17 | 0.03 |
| H(10) | 0.14 | -0.10 | 0.16 | H(23) | -0.08 | -0.04 | 0.20 |
| H(11) | 0.22 | -0.19 | 0.23 | H(24) | -0.38 | 0.18 | 0.20 |
| H(12) | 0.11 | -0.25 | 0.18 | H(25) | -0.44 | 0.23 | 0.13 |
| H(13) | -0.28 | 0.16 | 0.40 | | | | |

- 10.1 $z + 1.88 = 0$. The maximum deviation of any nitrogen atom from the plane is 0.006 ± 0.010 Å, indicating no significant deviation from planarity. The distances of the cation atoms from this plane are given in Table IV. All carbon and oxygen atoms are

 TABLE IV
 DISTANCES OF CATION ATOMS FROM LEAST-SQUARES PLANE

| Atom | Distance, Å | Atom | Distance, Å |
|------|-------------|-------|-------------|
| Ni | 0.0004 (15) | C(3) | 0.55 (1) |
| N(1) | 0.006 (10) | C(4) | 0.56 (1) |
| N(2) | 0.005 (10) | C(5) | 0.33 (1) |
| N(3) | 0.006 (10) | C(6) | 0.38 (1) |
| N(4) | 0.004 (10) | C(7) | 0.10 (1) |
| O(1) | 0.27 (1) | C(8) | 2.09 (1) |
| O(2) | 0.25 (1) | C(9) | 0.06 (1) |
| C(1) | 0.24 (1) | C(10) | 2.12 (1) |
| C(2) | 0.28 (1) | | |

out of the plane defined by the nickel and nitrogen atoms. The puckering puts all carbon atoms attached to nitrogens below the plane and both oxygens attached to oxime nitrogens above the plane.

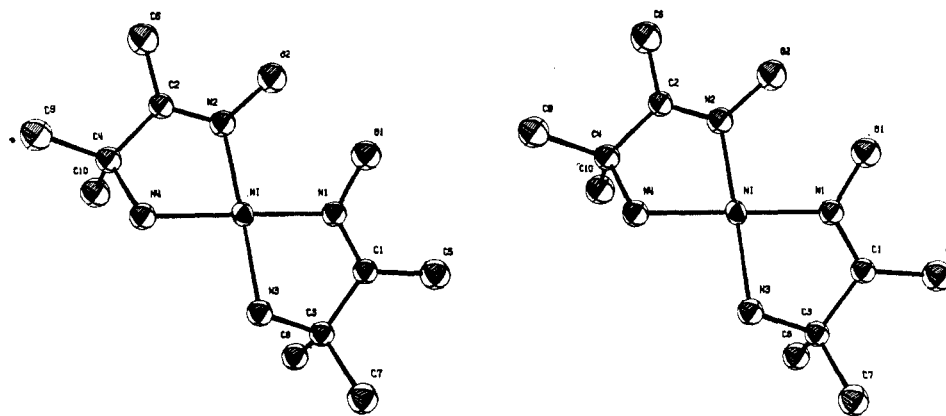
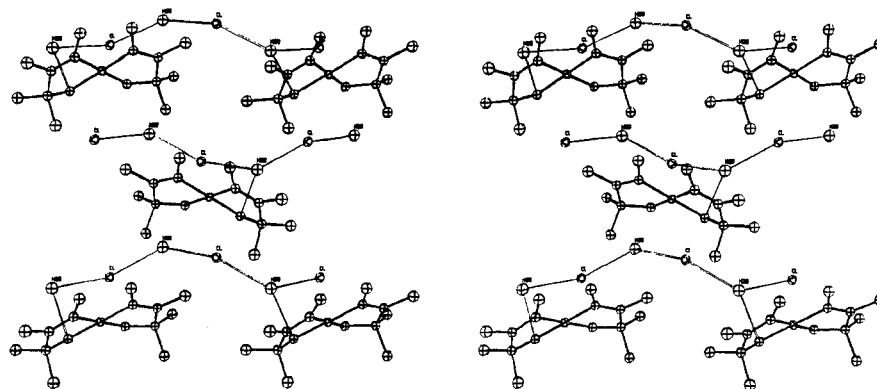


Figure 1.—Stereoscopic pair showing the structure of the bis(2-amino-2-methyl-3-butanone oximato)nickel(II) cation.

Figure 2.—View of one layer of cations, anions, and water molecules looking parallel to the a axis of the unit cell. The water hydrogen bonds are shown to indicate their relationship to the cations and the anions.

Looking parallel to the a axis (Figure 2), one encounters alternating double layers of cations and anions partially separated by layers of water molecules which link the anions together in chains by hydrogen bonds. Each water molecule is also hydrogen bonded to one of the amine nitrogens, N(4), of the cation. The closest contact of the anion to the cation involves contact of the chloride ion with the amine nitrogens, Cl-N(3) (3.26 and 3.39 Å) and Cl-N(4) (3.28 Å). Although the sum of the van der Waals radii of chlorine and nitrogen¹¹ is 3.3 Å, these distances do suggest hydrogen bonding of the chloride ion to the amine nitrogens. These Cl...N hydrogen bonds are not shown in Figure 2. The intermolecular angles (Table V) associated with the proposed hydrogen bonds appear to be reasonable. Each amine nitrogen is involved in two hydrogen bonds, N(3) to two chloride ions and N(4) to a chloride ion and a water molecule. Each chloride ion in turn is hydrogen bonded to two water molecules as well as to N(4) and to two N(3) atoms from different cations. The water molecule is hydrogen bonded (Figure 2) to two chloride ions and to N(4). The crystal structure is stabilized by this complex hydrogen-bonding network.

All intermolecular distances less than 4.0 Å are given in Table V. Contact distances between cations do not suggest any significant interaction. The shortest contact distances (3.40–3.54 Å) involve the oxime

(11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

TABLE V
INTERMOLECULAR DISTANCES^a

| Distance | Value, Å | Distance | Value, Å |
|-----------------------|----------|------------------------|----------|
| N(4)-H ₂ O | 2.92 (2) | C(5)-C(8) | 3.71 (2) |
| Cl-H ₂ O | 3.16 (1) | C(10)-H ₂ O | 3.73 (2) |
| Cl-H ₂ O | 3.19 (1) | C(5)-C(10) | 3.74 (2) |
| Cl-N(4) | 3.26 (1) | H ₂ O-C(9) | 3.77 (2) |
| Cl-N(3) | 3.30 (1) | H ₂ O-C(4) | 3.79 (2) |
| Cl-N(3) | 3.39 (1) | C(1)-C(6) | 3.82 (2) |
| O(1)-C(6) | 3.40 (2) | O(2)-C(10) | 3.82 (2) |
| O(1)-C(10) | 3.41 (2) | H ₂ O-N(3) | 3.84 (2) |
| O(1)-C(8) | 3.54 (2) | C(9)-H ₂ O | 3.85 (2) |
| Ni-H ₂ O | 3.61 (1) | C(2)-C(10) | 3.87 (2) |
| Cl-C(7) | 3.63 (2) | C(6)-C(10) | 3.87 (2) |
| N(1)-C(8) | 3.64 (2) | N(2)-C(10) | 3.88 (2) |
| O(2)-C(10) | 3.64 (2) | C(1)-C(7) | 3.91 (2) |
| C(7)-H ₂ O | 3.64 (2) | C(8)-C(9) | 3.92 (2) |
| O(1)-C(6) | 3.66 (2) | C(5)-C(6) | 3.94 (2) |
| O(2)-C(5) | 3.66 (2) | C(5)-C(9) | 3.94 (2) |
| C(1)-C(8) | 3.66 (2) | O(1)-O(2) | 3.98 (1) |
| N(1)-C(6) | 3.67 (2) | C(6)-C(8) | 3.99 (2) |

Intermolecular Angles^b

| Angle | Value, deg | Angle | Value, deg |
|------------------------------|------------|--|------------|
| H ₂ O...N(4)-Ni | 94.5 | Cl...N(3)-C(3) | 113.4 |
| Cl...N(4)-Ni | 106.6 | Cl...N(3)-C(3) | 127.3 |
| Cl...N(4)-C(4) | 123.1 | Cl...N(3)-Cl | 96.6 |
| H ₂ O...N(4)-C(4) | 113.8 | Cl...H ₂ O...Cl | 121.3 |
| H ₂ O...N(4)...Cl | 104.6 | Cl...H ₂ O...N(4) | 95.2 |
| Cl...N(3)-Ni | 102.2 | Cl...H ₂ O...N(4) | 141.7 |
| Cl...N(3)-Ni | 103.9 | H ₂ O...Cl...H ₂ O | 157.6 |

^a Standard deviations are in parentheses. ^b These angles are associated with the hydrogen bonds.

oxygens and methyl carbons and appear to be normal van der Waals contact distances (3.40 Å).¹¹ The shortest methyl carbon to methyl carbon distances (3.71 and 3.74 Å) are shorter than the sum of the van der Waals radii (4.0 Å), but no significant interaction between methyl groups is postulated.

The root-mean-square components of thermal displacement along the principal axes are given for the nickel and chlorine atoms in Table VI. The motion of the chlorine atom is within experimental error isotropic (Figure 2). The direction of maximum vibration of the nickel atom as might be expected is approximately perpendicular to the plane of the nickel and nitrogen atoms while the direction of minimum vibration is nearly in that plane and approximately parallel to a line connecting the two nitrogen atoms of one ligand.

TABLE VI

ROOT-MEAN-SQUARE COMPONENTS OF THERMAL DISPLACEMENT IN THE DIRECTION OF THE PRINCIPAL AXES (Å)^a

| Atom | Axis 1 | Axis 2 | Axis 3 |
|------|-----------|-----------|-----------|
| Ni | 0.153 (3) | 0.183 (3) | 0.187 (2) |
| Cl | 0.208 (5) | 0.215 (5) | 0.217 (5) |

^a Standard deviations are in parentheses.

Bond Distances and Angles.—The bond distances and angles are given in Table VII. The numbering system is shown in Figure 1. The average bond distances (Figure 3) are compared with those in related compounds in Table VIII.

TABLE VII

INTRAMOLECULAR DISTANCES AND ANGLES^a

| Distance | Value, Å | Angle | Value, deg |
|-----------------|------------|-----------------|------------|
| Ni-N(1) | 1.85 (1) | N(3)-Ni-N(4) | 95.8 (4) |
| Ni-N(2) | 1.86 (1) | Ni-N(1)-O(1) | 120.7 (8) |
| Ni-N(3) | 1.91 (1) | Ni-N(2)-O(2) | 122.4 (8) |
| Ni-N(4) | 1.91 (1) | O(1)-N(1)-C(1) | 120 (1) |
| N(1)-O(1) | 1.36 (1) | O(2)-N(2)-C(2) | 119 (1) |
| N(2)-O(2) | 1.35 (1) | Ni-N(1)-C(1) | 119.1 (8) |
| N(1)-C(1) | 1.31 (1) | Ni-N(2)-C(2) | 118.7 (8) |
| N(2)-C(2) | 1.29 (2) | N(2)-C(2)-C(6) | 123 (1) |
| C(1)-C(3) | 1.50 (2) | N(1)-C(1)-C(5) | 121 (1) |
| C(2)-C(4) | 1.49 (2) | N(1)-C(1)-C(3) | 114 (1) |
| C(1)-C(5) | 1.51 (2) | N(2)-C(2)-C(4) | 114 (1) |
| C(2)-C(6) | 1.50 (2) | C(3)-C(1)-C(5) | 124 (1) |
| C(3)-C(7) | 1.52 (2) | C(4)-C(2)-C(6) | 123 (1) |
| C(3)-C(8) | 1.56 (2) | C(1)-C(3)-N(3) | 106 (1) |
| C(4)-C(9) | 1.52 (2) | C(2)-C(4)-N(4) | 106 (1) |
| C(4)-C(10) | 1.57 (2) | C(1)-C(3)-C(7) | 113 (1) |
| C(3)-N(3) | 1.53 (2) | C(1)-C(3)-C(8) | 110 (1) |
| C(4)-N(4) | 1.51 (2) | C(2)-C(4)-C(9) | 113 (1) |
| O(1)-O(2) | 2.38 (1) | C(2)-C(4)-C(10) | 107 (1) |
| | | N(3)-C(3)-C(7) | 110 (1) |
| | | N(3)-C(3)-C(8) | 109 (1) |
| | | N(4)-C(4)-C(9) | 110 (1) |
| | | N(4)-C(4)-C(10) | 109 (1) |
| | | Ni-N(3)-C(3) | 110.6 (7) |
| | | C(7)-C(3)-C(8) | 110 (1) |
| | | Ni-N(4)-C(4) | 110.3 (7) |
| | | C(9)-C(4)-C(10) | 111 (1) |
| | | | |
| Angle | Value, deg | | |
| N(1)-Ni-N(2) | 97.7 (5) | | |
| N(1)-Ni-N(3) | 83.4 (4) | | |
| N(2)-Ni-N(4) | 83.1 (4) | | |
| C(7)-C(3)-C(8) | 110 (1) | | |
| C(9)-C(4)-C(10) | 111 (1) | | |

^a Standard deviations are in parentheses.

There are no significant differences between corresponding distances and angles in the two ligands, and within experimental error the symmetry of the cation (excluding hydrogen atoms) is C_s-m. The nickel to

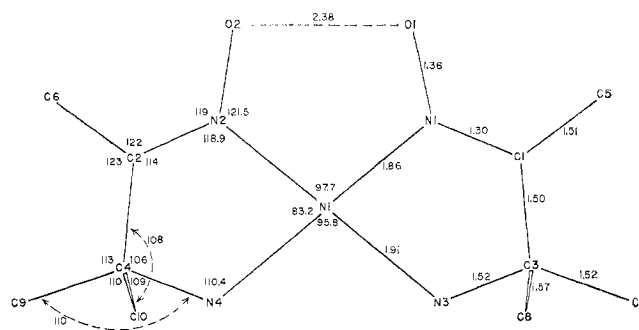


Figure 3.—Average bond angles and distances assuming C_s symmetry for the molecule.

TABLE VIII

COMPARISON OF AVERAGE INTRAMOLECULAR DISTANCES WITH THOSE OF RELATED COMPOUNDS

| Compound ^a | Distance | Value, Å | Ref |
|-------------------------------------|--------------------------------|----------|------|
| NiAO | C(tetra)-C(tetra) ^b | 1.54 (2) | c |
| NiAO | C(pl)-C(tetra) | 1.50 (2) | c |
| NiDMG | C(pl)-C(tetra) | 1.51 (2) | d |
| PdDMG | C(pl)-C(tetra) | 1.51 (4) | d, e |
| NiAO | C(tetra)-N(amine) | 1.52 (1) | c |
| Pd(en) ₂ Cl ₂ | C(tetra)-N(amine) | 1.47 (1) | f |
| NiAO | C(pl)-N(oxime) | 1.30 (1) | c |
| NiG | C(pl)-N(oxime) | 1.30 (1) | g |
| NiDMG | C(pl)-N(oxime) | 1.30 (1) | d |
| PdDMG | C(pl)-N(oxime) | 1.31 (1) | d, e |
| NiAO | N-O | 1.36 (1) | c |
| NiG | N-O | 1.35 (1) | g |
| NiDMG | N-O | 1.36 (1) | d |
| PdDMG | N-O | 1.35 (2) | d, e |
| NiAO | Ni-N(oxime) | 1.86 (1) | c |
| NiG | Ni-N(oxime) | 1.87 (1) | g |
| NiDMG | Ni-N(oxime) | 1.85 (1) | d |
| NiAO | Ni-N(amine) | 1.91 (1) | c |
| NiSd | Ni-N(amine) | 1.89 (1) | h |
| NiAO | O---O | 2.38 (1) | c |
| NiG | O---O | 2.45 (1) | g |
| NiDMG | O---O | 2.40 (2) | d |

^a NiAO = bis(2-amino-2-methyl-3-butanone oximate)nickel(II) chloride monohydrate; NiDMG = bis(dimethylglyoximate)nickel(II); PdDMG = bis(dimethylglyoximate)palladium(II); Pd(en)₂Cl₂ = bis(ethylenediamine)palladium(II) chloride; NiG = bis(glyoximate)nickel(II); and NiSd = bis(meso-stilbenediamine)nickel(II) dichloroacetate. ^b tetra = tetrahedral coordination; pl = trigonal-planar coordination. ^c This work. ^d See ref 1b. ^e See ref 3. ^f J. R. Wiesner and E. C. Lingafelter, *Inorg. Chem.*, **5**, 1770 (1966). ^g See ref 2. ^h See ref 12.

oxime nitrogen distances (1.86 Å) are significantly shorter than the nickel to amine nitrogen distances (1.91 Å) but are in good agreement with nickel-oxime nitrogen distances observed^{1,2} for other compounds (Table VII). The nickel-amine nitrogen distance is not significantly different from that observed for bis(meso-stilbenediamine)nickel(II) (1.89 Å).¹² The N-O distances (1.36 Å) and C-N(oxime) distances (1.30 Å) are also in good agreement with those found for the metal glyoxime compounds.¹⁻⁵ The C-C distances are normal. The C-N(amine) distances (1.52 Å) however appear to be significantly longer than those in bis(ethylenediamine)palladium(II) chloride (1.47 Å) and longer than the sum of the covalent radii (1.47 Å).¹³

(12) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, **3**, 468 (1964).

(13) See ref 11, p 224.

The intramolecular O...O distance (2.38 Å) is the shortest yet reported but within experimental error cannot be considered significantly shorter than that observed for nickel dimethylglyoxime (2.40 Å).¹ It does however appear to be significantly shorter than that observed for bis(glyoximato)nickel(II) (2.45 Å).² This shortening might be expected since the constraint imposed by the presence of two intramolecular hydrogen bonds is absent.

There is no significant deviation from 120° bond angles around N(1) and N(2). However, owing presumably to distortion resulting from coordination, the bond angles around C(1) and C(2) are significantly different from 120°. The bond angles around N(3), N(4), C(3), and C(4) are within experimental error identical and normal tetrahedral angles.

Since the distances involving hydrogen atoms are not accurately known, they are not included in Table VII. The four N-H distances range from 0.70 to 0.92 Å (average 0.84 Å); the 18 C-H distances, from 0.62 to 1.26 Å (average 0.92 Å); and the two O-H distances for the water molecule are 0.62 and 0.64 Å. The final hydrogen is 1.24 Å from O(1) and 1.22 Å from O(2). This hydrogen is not on the line connecting the two oxygen atoms, but rather the O-H-O angle is 157°. From the shape of the difference Fourier peak (Figure

4) it is not possible to decide whether this hydrogen atom has only one equilibrium position, but it does appear to be approximately at the symmetrical position. Definite location of the hydrogen atoms will be carried out by neutron diffraction.

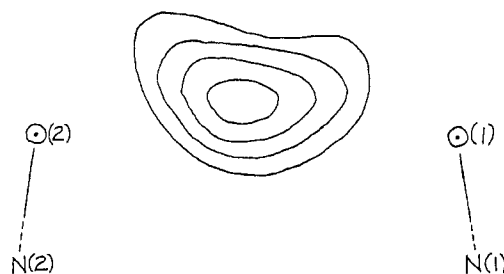


Figure 4.—A portion of the difference Fourier synthesis in the plane of the oxime nitrogen and oxygen atoms showing the hydrogen atom in the intramolecular hydrogen bond. The contours are drawn at 0.1 e⁻/Å³ intervals from 0.2 to 0.5 e⁻/Å³.

Acknowledgment.—The author gratefully acknowledges R. Kent Murmann for making available the crystals used in this study. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, EASTERN MONTANA COLLEGE, BILLINGS, MONTANA, AND THE DEPARTMENT OF CHEMISTRY, MONTANA STATE UNIVERSITY, BOZEMAN, MONTANA

The Crystal and Molecular Structure of Tin(IV) Chloride Glutaronitrile (SnCl₄NC(CH₂)₃CN)

By DAVID M. BARNHART,^{1a} CHARLES N. CAUGHLAN,^{1b} AND MAZHAR UL-HAQUE^{1b}

Received August 15, 1967

The structure of SnCl₄NC(CH₂)₃CN, tin(IV) chloride glutaronitrile, has been determined by an X-ray diffraction study. The crystals are orthorhombic, $a = 6.11$, $b = 12.90$, $c = 14.57$ Å, space group Pbcm; $D(\text{obsd})$ was 2.03 and $D(\text{calcd})$ was 2.05 on the basis of four asymmetric units per unit cell. The intensities of 656 independent reflections were recorded with a diffractometer. The structure was solved from the Patterson map and has been refined with a full-matrix least-squares refinement to a conventional R of 5.9%. The structure is in the form of a one-dimensional polymer with the glutaronitrile acting as a bridging ligand between the SnCl₄ units. The glutaronitrile is in the TT conformation. The tin is octahedrally coordinated with the nitrogen atoms in the *cis* configuration. The Sn-Cl distance is 2.35 ± 0.01 Å; the Sn-N distance is 2.29 ± 0.02 Å. The glutaronitrile distances appear normal.

Introduction

Complexes of dinitriles with tin(IV) have been described and characterized by Kubota and Schulze.^{2a} The complexes were believed to be polymers, with the dinitrile acting as a bridging ligand. This conclusion was arrived at as a result of the general properties, which were characteristic of polymeric substances, and by a consideration of the infrared spectra. The infrared spectra of complexes of glutaronitrile with a number

of metal ions were studied by Kubota and Johnston.^{2b} According to these authors, the spectra indicated the rotational conformer TT³ for the glutaronitrile in the tin(IV) complex, but spectral assignments for the TT conformer disagreed markedly with those designated by

(3) This notation, *trans,trans*, applies to rotational isomers of saturated hydrocarbons. One carbon atom is fixed in space and the directions of the four bonds around it are designated by a, b, c, d. A unique designation of the carbon skeleton can be obtained by denoting the directions of C-C bonds in order as a, b, c, or d. TT, *trans,trans*, is designated as abab; TG, *trans,gauche*, is abac; GG is abed, etc.: S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, N. Y., 1954, Part I, Chapter V.

(1) (a) Eastern Montana College; (b) Montana State University.

(2) (a) M. Kubota and S. R. Schulze, *Inorg. Chem.*, **3**, 853 (1964); (b) M. Kubota and D. L. Johnston, *J. Am. Chem. Soc.*, **88**, 2451 (1966).