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.
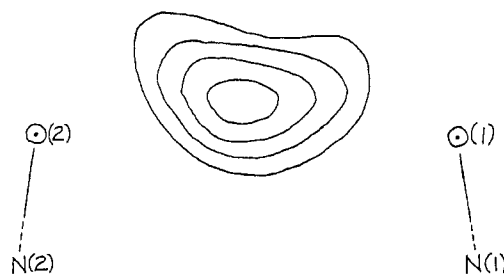

Figure 4.—A portion of the difference Fourier synthesis in the plane of the oxime nitrogen and oxygen atoms showing the hydrogen atom in the intramolecular hydrogen bond. The contours are drawn at 0.1 e⁻/Å³ intervals from 0.2 to 0.5 e⁻/Å³.

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]

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 TT[3] for the glutaronitrile in the tin(IV) complex, but spectral assignments for the TT conformer disagreed markedly with those designated by

(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).

(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 abcd, etc.: S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, N. Y., 1954, Part I, Chapter V.

Matsubara[4] in the pure glutaronitrile. This seems unusual since succinonitrile in complexes shows only slight shifts of the spectra from that of the pure compound. This X-ray crystal structure investigation was undertaken in order to determine with certainty the conformation of glutaronitrile in the tin(IV) complex, to aid in the assignment of the infrared frequencies, as well as to study further the coordination of nitrogen to tin(IV).

Experimental Section

$SnCl_4NC(CH_2)_3CN$ was prepared according to the method described by Kubota and Johnston.[2b] This consists of a dropwise addition of a dilute solution of gn (hereafter glutaronitrile is designated as gn) in benzene to a dilute solution of $SnCl_4$ in benzene. In very dilute solution crystallization proceeds slowly enough to yield small single crystals. Since the crystals are extremely hygroscopic, the reaction was carried out under a dry nitrogen atmosphere. Several crystals were transferred under dry nitrogen to capillaries, which were evacuated and sealed for microscopic and X-ray examination. A single crystal of approximate dimensions $0.1 \times 0.1 \times 0.2$ mm was selected for X-ray study. The lattice parameters were $a = 6.11 \pm 0.01$, $b = 12.90 \pm 0.06$, $c = 14.57 \pm 0.05$ Å. Space groups Pbcm or Pbc2$_1$ were indicated by systematic extinctions; $k \neq 2n$ for $0kl$ zone, $l \neq 2n$ for $h0l$ zone. Interpretation of the Patterson map and final refinement has indicated Pbcm. Each lattice parameter was calculated from measurements of diffraction angles on 8–10 reflections on the GE diffractometer, the uncertainty indicating standard deviations from these measurements. The density was measured on another crystal by flotation and was 2.03 g/cm³, compared with 2.05 g/cm³ calculated for four molecules per unit cell. The linear absorption coefficient for Cu Kα radiation which was used in collection of intensity data is 262.3 cm^{-1}.

The data were collected using a General Electric single-crystal orienter and spectrogoniometer equipped with a scintillation counter and pulse height analyzer for detector. The a axis was parallel to the ϕ axis of the single-crystal orienter. Independent reflections were collected by θ–2θ scan technique (moving-crystal–moving-counter method) using equal background and scan counting time. The background was counted on each side of the peak and averaged for calculation of intensities. The scan rate in 2θ was $1.80°$/min, the take-off angle was $4°$, and the counting time was 100 sec/scan for each background count. Nickel-filtered copper radiation was used. A total of 1449 reflections were scanned and 656 were found to be significantly above the statistical fluctuations of the background count. The data were corrected for Lorentz-polarization using an IBM 1620 computer.[5] For structure factor calculations, form factors used were from the literature[6] including the anomalous terms of the form factors in final cycles of refinement. Absorption corrections were made using a table look up program of Duane Swank and Roger Willet.[7] No extinction corrections were made since examination of structure factors did not indicate serious errors due to extinction.

Structure Determination and Results

From a three-dimensional Patterson map, correct tin and chlorine positions were found on the Harker section and a partial structure factor calculation provided phases for the first electron density map. Several structure factor calculations and electron density maps

(4) I. Matsubara, *J. Chem. Phys.*, **35**, 373 (1961); **34**, 1719 (1961).

(5) All programs used except the least-squares refinement are from the Montana State University Crystallographic Program Library written for the IBM 1620 Model II by C. N. Caughlan, C. T. Li, G. W. Svetich, K. D. Watenpaugh, and R. D. Witters.

(6) J. A. Ibers, "International Tables for Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, Table 3.3 1A.

(7) W. L. Bond, "International Tables for Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, Table 5.3.5B, pp 295–298.

were calculated before refinement was started. Refinement was carried out using the full-matrix least-squares program of Busing, Martin, and Levy[8] refining positional and anisotropic temperature factors minimizing $\Sigma w(|F_o| - |F_c|)^2$. Each observed reflection was given unit weight for refinement. Two cycles of re-

TABLE I
ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS

Atom	x	y	z
Sn(1)	-0.1604 (3)^a	0.5259 (1)	0.2500 (–)
Cl(2)	0.0102 (17)	0.3626 (6)	0.2500 (–)
Cl(3)	-0.4217 (12)	0.6599 (5)	0.2500 (–)
Cl(4)	0.0407 (8)	0.5900 (4)	0.3761 (3)
N(5)	-0.3983 (23)	0.4473 (12)	0.3495 (10)
C(6)	-0.5125 (33)	0.3944 (15)	0.3921 (11)
C(7)	-0.3522 (34)	0.3276 (13)	0.4484 (11)
C(8)	-0.4987 (49)	0.2500 (–)	0.5000 (–)

^{a} The number in parentheses is the standard deviation and refers to the least significant digit.

TABLE II
THERMAL PARAMETERS AND MEAN-SQUARE DISPLACEMENT

	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)	MAX	MED	MIN
Sn(1)	2.5	2.8	1.3	-0.1	0.0	0.0	0.04	0.03	0.02
Cl(2)	5.9	3.8	4.3	2.3	0.0	0.0	0.09	0.05	0.03
Cl(3)	3.5	3.0	3.6	0.5	0.0	0.0	0.05	0.05	0.03
Cl(4)	3.4	6.4	2.2	-0.5	0.6	1.0	0.08	0.05	0.02
N(5)	3.1	4.3	2.8	0.1	1.0	-1.2	0.06	0.04	0.02
C(6)	3.1	4.8	1.8	-1.1	0.1	-0.5	0.07	0.03	0.02
C(7)	3.3	3.4	2.8	0.1	-0.1	-1.7	0.06	0.04	0.02
C(8)	2.9	3.3	2.6	0.0	0.0	-1.3	0.05	0.04	0.02

(These are given as B_{ij}'s rather than β_{ij}'s)   Mean Square Displacement Å^2

TABLE III
INTERATOMIC DISTANCES

Atoms	Bond, Å
Sn(1)–Cl(2)	2.35 (1)^a
Sn(1)–Cl(3)	2.35 (1)
Sn(1)–Cl(4)	2.36 (1)
Sn(1)–N(5)	2.29 (2)
N(5)–C(6)	1.16 (4)
C(6)–C(7)	1.54 (4)
C(7)–C(8)	1.54 (4)

^{a} The number in parentheses is the standard deviation and refers to the least significant digit.

TABLE IV
BOND ANGLES

Atoms	Angle, deg
Cl(2)–Sn(1)–Cl(3)	163.6 (2)^a
Cl(2)–Sn(1)–Cl(4)	94.8 (1)
Cl(2)–Sn(1)–N(5)	83.3 (1)
Cl(3)–Sn(1)–Cl(4)	95.5 (2)
Cl(3)–Sn(1)–N(5)	84.0 (2)
Cl(4)–Sn(1)–N(5)	89.5 (2)
Sn(1)–N(5)–C(6)	169.8 (11)
N(5)–C(6)–C(7)	103.5 (13)
C(6)–C(7)–C(8)	104.8 (11)
C(7)–C(8)–C(7')	108.9 (8)

^{a} The number in parentheses is the standard deviation and refers to the least significant digit.

finement, refining positional parameters and isotropic temperature factors, and two cycles, refining positional parameters and anisotropic temperature factors, including the anomalous terms of the scattering factors in the

(8) W. R. Busing, K. D. Martin, and H. A. Levy, ORFLS, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

TABLE V
OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

[a] The columns reading from left to right contain the value of l, F_o, F_c.
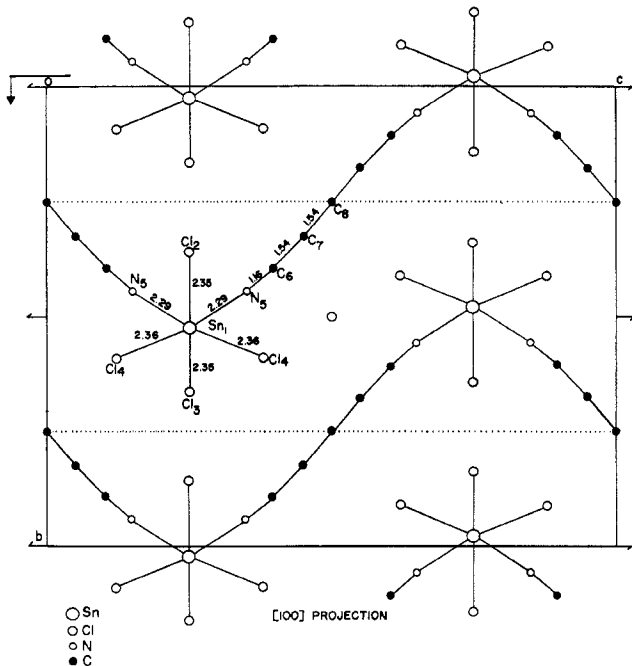
Figure 1.—Projection of the structure of tin chloride glutaronitrile projected down the a axis.
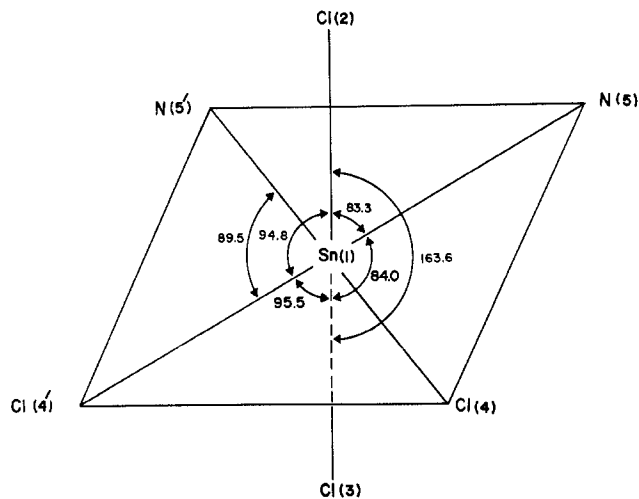
○ Sn
○ Cl
○ N
● C

[100] PROJECTION

Figure 2.—Coordination and bond angles around tin in tin chloride glutaronitrile.

the structure, and Figure 2 indicates in more detail the coordination around the tin atom.

Discussion of the Structure

It can be seen from Figure 1 that the glutaronitrile molecule acts as a bridging ligand between the tin chloride molecules; this results in a one-dimensional polymer in the direction of the c axis. The glutaronitrile is in the TT conformation and is nearly planar. The best least-squares plane is described by the equation $0.0000X + 0.6457Y + 0.7636Z = 7.6269$.[9] The maximum devia-

last cycle, have reduced the conventional R factor to 5.9%. Inclusion of the anomalous terms made an insignificant improvement. A final difference map showed no significant features. Final positional parameters with standard deviations are listed in Table I. Table II gives anisotropic temperature factors and mean-square displacement. Table III shows the interatomic distances, and Table IV gives the bond angles. Table V shows calculated and observed structure factors. Figure 1 shows the projection down the a axis of

tion from this plane is 0.07 Å. It should be noted that C(8) sits on the twofold axis so that half of the glutaronitrile molecule is related to the other half by the twofold symmetry.

The tin is octahedrally coordinated, the nitrogen atoms being in the *cis* configuration. Examination of Figure 2 indicates that the octahedron is somewhat, although not greatly, distorted. Sn, N(5), N(5'), Cl(4), and Cl(4') are nearly planar, the best least-squares plane being described by the equation $-0.3240X + 0.9461Y + 0.0000Z = 7.2514$; maximum deviations of any atoms from this plane are only about 0.01 Å. Also, Sn, Cl(2), Cl(3), Cl(4), and N(5) are close to being planar, the equation being $0.3362X + 0.4679Y + 0.8173Z = 5.2602$, with Sn being about 0.2 Å from this plane.

The Sn–Cl distance of 2.35 ± 0.01 Å agrees well with those in $SnCl_4(OSeCl_4)_2$, *i.e.*, 2.36 and 2.41 Å.[10] In $SnCl_4(OSeCl_4)_2$ the octahedron around tin is slightly more distorted than in $SnCl_4(gn)$. In benzaldeminium stannichloride[11] the $SnCl_6{}^{2-}$ ion shows three distances, 2.42, 2.50, 2.54 Å, all of which are somewhat longer

than those in $SnCl_4(gn)$. The distance shown in $SnCl_4$ gas by electron diffraction is 2.31 ± 0.01 Å,[11] this of course being a tetrahedral molecule. No Sn–N distances are available for comparison.

Thus the conformation of the glutaronitrile as TT has been confirmed, and it has been shown that this complex is, in fact, a one-dimensional polymer. There is no immediately obvious explanation of the difference in spectral assignments for the glutaronitrile in the tin-(IV) complex from those in the pure glutaronitrile.

(10) Y. Hermodsson, *Acta Cryst.*, **13**, 656 (1960).

(11) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Supplement Special Publication No. 18, The Chemical Society, London, 1965, p M22S.

Ligand Preferences of Transition Metals in Complexes as Determined from Nuclear Magnetic Resonance Contact Shifts

By DENIS FORSTER, KURT MOEDRITZER, and JOHN R. VAN WAZER

The Fermi contact term causes a large change in the nuclear magnetic resonance chemical shift of a nucleus in a ligand bonded to a paramagnetic transition metal atom as compared to the same ligand in the free state. When there is rapid exchange of ligand between the free state and the metal complex(es), the variation in the position (depending on the ratio of free to coordinated ligand) of the resonance is large so that for ligand mixtures a reasonably precise measurement may be obtained of the fraction for each kind of ligand which is coordinated. From data of this type, the competitive equilibria for coordination of nickel by pyridine *vs.* α-, β-, or γ-picoline, picoline oxide, triphenylphosphine, or triphenylphosphine oxide were investigated. An equilibrium constant for treating these data is derived and applied to the appropriate systems.

The literature[1] dealing with labile replacement of one ligand by another on transition metals has been essentially limited to spectral studies involving mixtures of molecules which exhibit appreciably different electronic transitions. Thus these studies, based on electronic spectra as well as on a few other techniques such as nuclear magnetic resonance (nmr), are generally limited to pairs of ligands involving coordination through two different elements. By the technique described herein, it is possible to make reasonably precise measurements on systems in which the rapidly exchanging, competing ligands are very similar.

For diamagnetic systems, it is generally found that

the nmr chemical shift of a magnetically active nucleus which is part of a ligand is not very different in the complex as compared to the free state, except when the nucleus is directly bonded to the acceptor atom. When the acceptor is a paramagnetic atom,[2] delocalization of the unpaired electron(s) into the ligand orbitals leads to a large difference in shift between the coordinated and free ligand, with delocalization into the ligand σ orbitals causing downfield shifts as large as several hundred parts per million and delocalization into the π orbitals usually giving severalfold smaller shifts which alternate in sign in a conjugated system. This led us to consider the applicability to paramagnetic systems of a quantitative treatment of the shifts of the

(1) *E.g.*, A. E. Harvey and D. L. Manning, *J. Amer. Chem. Soc.*, **72**, 4488 (1950).

(2) D. R. Eaton and W. D. Phillips, *Advan. Mag. Resonance*, **1**, 103 (1965).