constant using total concentrations. The ratio of eq. 16 to 17 yields

$$\frac{(NO_3)P_{H_2}^{1/2}}{(H^+)(NO_3^-)} = \frac{k_2}{k_1(NO_3^-)K_a} \qquad (18)$$

which is the equilibrium constant for the reaction

$$H^+ + NO_3^- = NO_3 + {}^1/_2H_2(g) \qquad (19)$$

All of the quantities on the right of eq. 18 are known or can be estimated at 50°. From ref. 2 we calculate $k_1 = 1.96 \times 10^6$, and from ref. 3 we find $k_2 = 1.33 \times 10^{-5}$. The value of K_a can be calculated from the formal potential, measured at 50°, of the Ce(III)–Ce(IV) half-cell in 6 F HNO_3 relative to the standard hydrogen half-cell. This latter value is not known with certainty. However, the work of Noyes and Garner[6] indicates that the variation of this potential with temperature is less than 0.01 v. when temperature is changed from 0 to 25° for a medium consisting of 1 F HNO_3 and 1 F $HClO_4$. This observation, coupled with the measurements of Smith,[7] leads us to estimate the formal potential of 6 F HNO_3 at 50° to be 1.59 ± 0.02 v. The value of K_a is then found to be 6.6×10^{24}, and the value of the equilibrium constant for reaction 19 is 1.7×10^{-37}. This value yields a free energy of reaction of 54.4 kcal. and an $E°$ for the half-reaction $NO_3^- = NO_3 + e^-$ of −2.35 v. at 50°. Finally, with the aid of the free energy of formation[8] of aqueous HNO_3, calculated to be −32.79 kcal. at 50°, we obtain the free energy of formation of aqueous NO_3 radical at 50° to be 21.6 kcal.

Our numerical results are, of course, based on the assumption that the intermediate in the Ce(IV)–Tl(I) reaction is NO_3. If the intermediate is actually OH, we would conclude that the thermal rate of formation of NO_3 is less than that for OH and therefore the equilibrium constant in eq. 18 would be smaller than that calculated above, giving a larger value for the free energy of reaction 19 and a larger value for the free energy of formation of aqueous NO_3. Our value of 21.6 kcal. is therefore seen to be a lower limit. Independent evaluations of this quantity are underway.

Acknowledgment. We are indebted to Dr. Richard J. Kokes for valuable discussions.

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Crystal and Molecular Structure of Bis(N-isopropylsalicylaldiminato)copper(II)

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Abstract: The crystal structure of bis(N-isopropylsalicylaldiminato)copper(II), $(C_3H_7N{=}CHC_6H_4O)_2Cu$, has been determined by X-ray diffraction analysis. The crystals are orthorombic, space group Pbca. Cell dimensions are $a = 12.87 \pm 0.04$, $b = 20.68 \pm 0.03$, $c = 14.58 \pm 0.03$ Å.; $Z = 8$. The coordination around the copper atom is a flattened tetrahedron with symmetry C_2. The angle between the planes defined by the Cu–N-1–O-1 and Cu–N-2–O-2 groups is about 60°.

It has been reported[1] that bis(N-isopropylsalicylaldiminato)copper(II), $(C_3H_7N{=}CHC_6H_4O)_2Cu$, is nearly, but not perfectly isomorphous with the analogous nickel complex, which was shown to be tetrahedral by means of magnetic, spectrophotometric, and molecular weight measurements.[2] A recent three-dimensional X-ray analysis[3] has confirmed the nickel complex to have a tetrahedral structure, although slightly distorted.

It is concluded that the copper atom has in bis(N-isopropylsalicylaldiminato)copper(II) a similar, but somewhat distorted, configuration.

It has been independently reported[4] that copper complexes with N-alkylsalicylaldimines can occur in tetrahedral or planar configurations, depending on the nature of the alkyl group and of the ring substituents, and that these structures can be recognized on the basis of their ultraviolet and visible spectra.[4a] Recently, the structure of bis(N-*t*-butylsalicylaldiminato)-copper(II)[5] has been studied by X-ray analysis and found to be a distorted tetrahedron, as suggested on the basis of its reflectance spectrum.[4a]

In order to provide some precise information about the structure of bis(N-isopropylsalicylaldiminato)copper(II), we have undertaken a three-dimensional X-ray analysis.

Experimental Section

Bis(N-isopropylsalicylaldiminato)copper(II) was prepared by the reaction between bis(salicylaldehydato)copper(II) and isopropylamine in methanol.

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Table I. Positional Parameters, Temperature Factors, and Their Estimated Standard Deviations

Atom	x/a	$\sigma_x \times 10^5$	y/b	$\sigma_y \times 10^5$	z/c	$\sigma_z \times 10^5$	B, Å.^{2}	σ_B, Å.^{2}
Cu	0.0613	16	0.1938	5	0.1253	8	3.80	0.03
O-1	0.0563	75	0.2762	30	0.1778	44	4.31	0.17
O-2	0.1493	75	0.1199	30	0.1370	41	4.49	0.16
N-1	−0.0645	89	0.1622	37	0.1845	52	3.77	0.21
N-2	0.1127	99	0.2159	37	−0.0005	54	4.21	0.20
C-1	−0.0192	113	0.3010	38	0.2264	57	3.11	0.24
C-2	−0.0055	111	0.3659	41	0.2593	64	3.72	0.22
C-3	−0.0880	137	0.3945	57	0.3108	83	5.34	0.46
C-4	−0.1821	135	0.3624	56	0.3286	83	4.73	0.48
C-5	−0.1934	121	0.2988	44	0.2977	68	4.04	0.30
C-6	−0.1112	105	0.2671	38	0.2478	64	3.04	0.20
C-7	−0.1312	118	0.2009	41	0.2274	60	3.55	0.24
C-8	−0.1036	135	0.0934	52	0.1792	78	5.05	0.42
C-9	−0.0881	148	0.0696	62	0.0783	91	7.63	0.62
C-10	−0.0307	132	0.0540	54	0.2461	87	5.79	0.44
C-11	0.2083	129	0.0946	51	0.0710	75	4.22	0.38
C-12	0.2613	121	0.0364	46	0.0931	67	4.40	0.27
C-13	0.3278	130	0.0076	54	0.0288	76	5.39	0.44
C-14	0.3396	150	0.0340	65	−0.0579	95	6.29	0.77
C-15	0.2892	135	0.0900	54	−0.0814	80	5.22	0.44
C-16	0.2206	119	0.1221	45	−0.0177	65	4.21	0.29
C-17	0.1712	121	0.1797	49	−0.0467	72	4.61	0.32
C-18	0.0706	129	0.2731	52	−0.0496	78	6.95	0.43
C-19	0.1387	107	0.3297	40	−0.0318	59	7.68	0.22
C-20	−0.0452	145	0.2827	64	−0.0294	94	6.38	0.66

Suitable crystals were grown from chloroform solution. Cell dimensions were determined from rotation photographs about the three principal crystallographic axes. The values obtained were $a = 12.87 \pm 0.04$, $b = 20.68 \pm 0.03$, $c = 14.58 \pm 0.03$ Å.; $Z = 8$. The calculated density was 1.33 g. cm.$^{-3}$. Systematic absences of ($0kl$) for k odd, ($h0l$) for l odd, and ($hk0$) for h odd indicated the space group to be Pbca. Multiple film equi-inclination Weissenberg photographs $0kl$ through $6kl$ were taken on a Nonius integrating Weissenberg camera, with Ni-filtered Cu Kα radiation (λ 1.5418 Å.).

The crystal chosen for collection of intensities was a plate having dimensions 0.50 × 0.15 × 0.30 mm. The intensities of the double integrated diffraction spots were measured on a Nonius microdensitometer, the density being assumed proportional to the intensity of the reflections.

Of the 1740 independent reflections examined, 1075 had measurable intensities and 665 were too weak to be measured. Intensities were corrected for Lorentz and polarization factors. No correction was made for absorption nor for spot elongation on upper levels. The reflections (020), (023), (131), (112), (220), (212), (202), (230), and (341) were later considered to be affected by secondary extinction. These reflections were omitted from the least-squares refinement and in the calculation of the final R factor.

The atomic scattering factors listed in "International Tables for X-ray Crystallography"[6] were used in the calculations. The atomic scattering factor of copper was corrected for the real part of the anomalous dispersion ($\Delta f' = -2.1$ for Cu Kα).

All calculations were carried out on an IBM 1620, with a set of programs written at the University of Bari.[7]

Determination of the Structure. Initial coordinates for the atoms were taken from the known structure of the isomorphous Ni(II) complex.[3] Input R was 43.4% with isotropic temperature factors as follows (in Å.^{2}): 2.00 for copper, 2.50 for nitrogen and oxygen, and 3.00 for carbon. R is throughout defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, where the sums are over the independent, observed reflections.

Two three-dimensional Fourier syntheses gave shifts in the atomic coordinates which reduced the R factor to 19.8%.

Refinement was continued by means of several cycles of least squares, using the block diagonal approximation and individual isotropic temperature factors. Variable weights were assigned to the observed structure factors according to the function $w = 1/(a + F_o + cF_o^2)$, where a and c were given the values of 20.00 and 0.01, respectively. Unobserved reflections, which were included in the last three cycles with half the minimum observable F_o value, were given constant weight adjusted to give an average $w\Delta^2 = 1$.[8] Weights in the last cycle ranged from 0.0019 to 0.0329 for observed reflections and had a constant value of 0.0166 for unobserved reflections. The function minimized was $\Sigma w||F_o| - |F_c||^2$.

Refinement was discontinued when all shifts in coordinates and temperature factors were less than the standard deviations. The R factor, with the parameters from the last cycle, was 11.0%.

The final values of the coordinates and temperature factors and their estimated standard deviations are given in Table I.

At this point a three-dimensional difference synthesis was calculated in order to locate hydrogen atoms. Although the synthesis showed other peaks of equal height, electron density peaks were found in geometrically reasonable positions and attributed to hydrogen atoms. In this way, 18 out of the 24 hydrogen atoms were located and their coordinates are shown in Table II.

Table II. Coordinates of Hydrogen Atoms

Atom	x/a	y/b	z/c
H-2	0.026	0.388	0.214
H-3	−0.090	0.450	0.330
H-4	−0.240	0.390	0.380
H-5	−0.254	0.263	0.296
H-7	−0.300	0.177	0.244
H′-9	−0.116	0.098	0.044
H′′-9	−0.130	0.016	0.046
H′-10	−0.020	0.075	0.310
H′′-10	0.060	0.029	0.252
H′′′-10	−0.046	−0.007	0.246
H-12	0.240	0.013	0.150
H-13	0.360	−0.025	0.066
H-14	0.300	−0.023	−0.084
H-15	0.278	0.120	−0.136
H-17	0.196	0.198	−0.120
H′-19	0.100	0.380	−0.050
H′′-19	0.172	0.330	−0.094
H′-20	−0.080	0.240	−0.052

The hydrogen atoms are numbered according to the carbon atoms to which they are attached. The average peak height was 0.4 electron Å.$^{-3}$ and the average C–H distance 1.10 Å.

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(6) "International Tables for X-ray Crystallography," Vol. II, Kynoch Press, Birmingham, 1962.

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Introduction of the hydrogen coordinates, with an isotropic temperature factor of 4.5 Å.^{2} reduced the R factor to 10.5%.[9]

Description of the Structure. The atomic arrangement in the molecule is shown in Figure 1. Bond lengths and angles around the copper atom are listed in Table III with their estimated standard deviations.

Table III. Bond Lengths and Angles about the Copper Atom with Their E.s.d.'s

Bond	Length, Å.	σ, Å.
Cu-O-1	1.870	0.006
Cu-O-2	1.887	0.007
Cu-N-1	1.979	0.010
Cu-N-2	1.990	0.008
Angle	**Angle, deg.**	**σ, deg.**
N-1-Cu-N-2	137.7	0.4
O-1-Cu-O-2	137.1	0.4
N-1-Cu-O-1	94.4	0.4
N-2-Cu-O-2	95.0	0.4
N-1-Cu-O-2	100.3	0.4
N-2-Cu-O-1	100.7	0.3

As expected from the isomorphism with the nickel analog, the coordination configuration around the copper is that of a distorted tetrahedron. However the distortion from the tetrahedral stereochemistry is much greater than in the nickel complex. It is interesting to note that in the case of copper, the coordination tetrahedron has symmetry C_2 within two standard deviations. The angle between the planes containing the Cu-N-1-O-1-and Cu-N-2-O-2 groups is 59° 40′. This same angle was 81° 30′ in the nickel complex.

If we assume this angle as a measure of the flattening of the tetrahedron, we can arrange the four-coordinated copper chelates, whose structures have been so far elucidated by X-ray analysis, in the order shown in Table IV.

Table IV. Variation of the Angle Between the Coordination Planes in Four-Coordinated Copper Chelates

Angle, deg.	Complex	Ref.
90	None	. . .
80[a]	Bis (N-*t*-butylsalicylaldiminato)copper(II)	5
60	Bis(N-isopropylsalicylaldiminato)copper(II)	Present work
43[a]	2,2′-Biphenylbis(2-iminomethylphenolato)copper(II)	*b*
0	Bis(N-phenylsalicylaldiminato)copper(II) (and other planar copper complexes)	11

[a] The value given by the authors and reported here is actually the angle between the salicylaldimine planes. [b] T. P. Cheeseman, D. Hall, and T. M. Waters, *Proc. Chem. Soc.*, 379 (1963).

The Cu-N distance (mean value 1.98 Å.) is 0.1 Å. longer than the Cu-O distance (mean value 1.88 Å.) as found in most metal salicylaldiminates. The Cu-O distance of 1.88 Å. and Cu-N distance of 1.98 Å. are similar to the 1.90 and 1.99 Å. in bis(N-methylsalicylaldiminato)copper(II)[10] and to the 1.88 and 1.99 Å. in bis(N-phenylsalicylaldiminato)copper(II),[11] both of which were found to be square-planar.

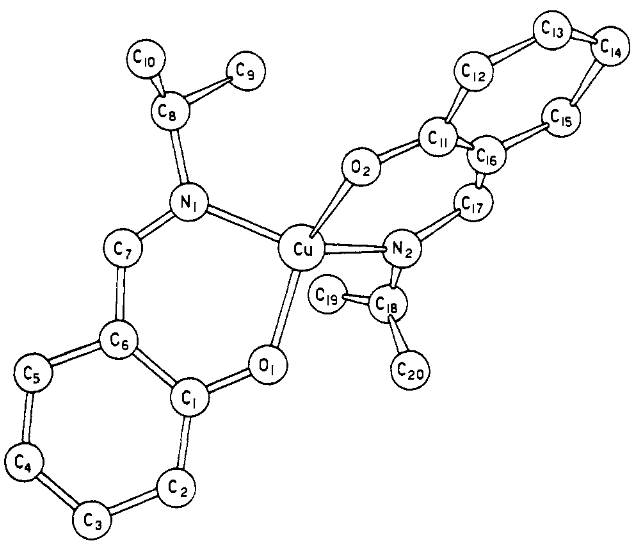

Figure 1. The atomic arrangement in the molecule of bis(N-isopropylsalicylaldiminato)copper(II).

This behavior is different from that observed in bis(N-isopropylsalicylaldiminato)copper(II), where the metal-ligand distances are about 0.1 Å. longer than the corresponding distances in planar nickel(II) salicylaldiminates.

Bond lengths and angles in the salicylaldimine residues are listed in Tables V and VI with their estimated standard deviations.

Table V. Intramolecular Distances in the Salicylaldimine Groups and Their E.s.d.'s

Bond	d, Å.	σ, Å.	Bond	d, Å.	σ, Å.
C-1-C-2	1.436	0.011	C-11-C-12	1.420	0.016
C-2-C-3	1.428	0.019	C-12-C-13	1.402	0.018
C-3-C-4	1.405	0.022	C-13-C-14	1.385	0.017
C-4-C-5	1.397	0.014	C-14-C-15	1.370	0.019
C-5-C-6	1.441	0.017	C-15-C-16	1.443	0.018
C-6-C-1	1.410	0.017	C-16-C-11	1.421	0.014
C-6-C-7	1.424	0.012	C-16-C-17	1.414	0.015
C-1-O-1	1.307	0.014	C-11-O-2	1.332	0.014
C-7-N-1	1.329	0.015	C-17-N-2	1.257	0.015
N-1-C-8	1.511	0.014	N-2-C-18	1.485	0.014
C-8-C-9	1.564	0.017	C-18-C-19	1.485	0.016
C-8-C-10	1.579	0.019	C-18-C-20	1.532	0.024
C-9-O-2	3.339	0.020	C-19-O-1	3.418	0.011
C-9-C-7	3.522	0.015	C-19-C-17	3.137	0.013
C-10-O-2	3.123	0.017	C-20-O-1	3.294	0.016
C-10-C-7	3.313	0.015	C-20-C-17	3.515	0.021
C-8-O-2	3.357	0.019	C-18-O-1	3.321	0.013

In Table VII are listed the coefficients of the equations of the various least-squares planes, and in Table VIII are the distances from the least-squares planes of the salicylaldimine residues.

As found in the analogous nickel complex and in other copper(II) and nickel(II) salicylaldiminates, the metal atom is out of the planes of the salicylaldimine groups, the distance from the plane being 0.17 Å. in one case and 0.08 Å. in the other.

An unexpected result is the considerable deviation from planarity of salicylaldimine I. In this salicylaldimine the chelate group has been twisted away from the plane in the way to restore some planarity to the coordination arrangement. In fact, the angle between the plane of salicylaldimine II and the plane defined by the benzene ring of salicylaldimine I, is 64° 42′, that is about 5° greater than the angle between the coordination planes.

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(9) Calculated and observed structure factors are deposited as Document No. 8598 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting $2.50 for photoprints or $1.75 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(10) E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, **14**, 1222 (1961).

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Table VI. Bond Angles in the Salicylaldimine Groups and Their E.s.d.'s

Angle	∠, deg.	σ, deg.	Angle	∠, deg.	σ, deg.
O-1–C-1–C-6	123.3	0.8	O-2–C-11–C-16	124.3	1.0
O-1–C-1–C-2	117.1	1.1	O-2–C-11–C-12	116.2	0.9
C-6–C-1–C-2	119.6	1.0	C-16–C-11–C-12	119.5	1.1
C-1–C-2–C-3	118.1	1.2	C-11–C-12–C-13	120.1	1.0
C-2–C-3–C-4	122.8	1.1	C-12–C-13–C-14	120.6	1.2
C-3–C-4–C-5	118.3	1.3	C-13–C-14–C-15	120.6	1.4
C-4–C-5–C-6	120.9	1.3	C-14–C-15–C-16	121.1	1.1
C-5–C-6–C-1	120.1	0.8	C-15–C-16–C-11	118.0	1.0
C-5–C-6–C-7	114.2	1.1	C-15–C-16–C-17	118.0	0.9
C-1–C-6–C-7	125.7	1.1	C-11–C-16–C-17	123.9	1.1
C-6–C-7–N-1	124.0	1.2	C-16–C-17–N-2	127.6	1.0
C-7–N-1–C-8	112.1	1.1	C-17–N-2–C-18	115.8	0.9
N-1–C-8–C-10	104.8	1.1	N-2–C-18–C-20	111.4	1.1
N-1–C-8–C-9	107.6	0.9	N-2–C-18–C-19	109.2	1.1
C-9–C-8–C-10	110.0	1.1	C-19–C-18–C-20	116.0	1.0
C-1–O-1-Cu	128.3	0.7	C-11–O-2–Cu	125.6	0.6
C-7–N-1–Cu	123.1	0.7	C-17–N-2–Cu	123.0	0.7
C-8–N-1–Cu	124.6	0.8	C-18–N-2–Cu	121.0	0.8

Table VII. Coefficients of Least-Squares Plane Equations, $Ax + By + Cz = d$ (x, y, z in Å.)

	A	B	C	d
I Salicylaldimine	0.3999	−0.3191	0.8591	0.7937
Coordination	0.5337	−0.3195	0.7830	0.5917
Isopropyl	0.7232	0.6785	−0.1289	0.0093
II Salicylaldimine	0.7749	0.5357	0.3355	3.4788
Coordination	0.7328	0.5666	0.3766	3.5654
Isopropyl	−0.1434	0.3153	−0.9381	2.3291

The planes defined by the carbon atoms of the isopropyl groups are nearly normal to the planes of the salicylaldimine groups to which they are attached.

Table VIII. Distances from Least-Squares Planes of Salicylaldimine Residues

	d, Å.		d, Å.
C-1	−0.043	C-11	−0.006
C-2	0.011	C-12	−0.014
C-3	0.043	C-13	0.015
C-4	−0.007	C-14	0.001
C-5	−0.032	C-15	0.004
C-6	−0.025	C-16	−0.013
C-7	0.053	C-17	−0.009
N-1[a]	0.115	N-2	0.012
O-1[a]	−0.099	O-2	0.009
Cu[a]	−0.172	Cu[a]	−0.077

[a] Atoms not included in the calculation of the least-squares plane.

Table IX. Intermolecular Distances Less than 3.8 Å.

Atom 1[a]	Atom 2	Distance	Molecule Position
C-15	C-3	3.713	$x + 1/2, 1/2 - y, \bar{z}$
C-15	C-4	3.754	$x + 1/2, 1/2 - y, \bar{z}$
C-15	C-20	3.752	$x + 1/2, 1/2 - y, \bar{z}$
C-16	C-20	3.665	$x + 1/2, 1/2 - y, \bar{z}$
C-17	C-2	3.749	$x, 1/2 - y, z - 1/2$
C-18	C-1	3.788	$x, 1/2 - y, z - 1/2$
C-20	C-5	3.582	$x, 1/2 - y, z - 1/2$
C-20	C-6	3.512	$x, 1/2 - y, z - 1/2$
C-20	C-7	3.730	$x, 1/2 - y, z - 1/2$
O-1	C-5	3.274	$1/2 + x, y, 1/2 - z$
C-12	C-10	3.577	$1/2 + x, y, 1/2 - z$

[a] In x, y, z.

In Table IX are listed the intermolecular distances less than 3.8 Å. All these distances appear to be normal.

The Nature of the Chemical Bond in Lithium Hydride and Hydrogen Fluoride

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Abstract: The Hartree–Fock charge distributions for the LiH and HF molecules are examined from the point of view of the forces they exert on the nuclei. The density resulting from each molecular orbital is classified either as binding, nonbinding, or antibinding with respect to the forces it exerts on the nuclei. In addition, whether the bonding in these molecules is primarily ionic or covalent in character is also determined, since these two extremes of bonding exhibit very characteristic features in their density distributions and in the nature of the forces exerted on the nuclei.

Hartree–Fock wave functions have been determined for the LiH and HF molecules.[2,3] A Hartree–Fock wave function yields a one-electron density distribution which is correct to the second order,[4] and thus such a density and its dependent properties can provide a reliable description of a chemical bond. The forces which are exerted on a nucleus in a molecule are determined by the one-electron density distribution, and we choose this property together with the density distribution itself to obtain an understanding of the binding in a molecule. We have previously applied

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