intensity standards showed a loss in intensity of 12.5%, a decay correction was applied. Systematic extinctions ($h0l$, $l \neq 2n$) were consistent with the space group $P2/c$. The structure was solved by the Patterson method. Full-matrix least-squares refinement[16] and difference Fourier calculations were used to locate all remaining non-hydrogen atoms including a solvent toluene molecule. Positions of hydrogen atoms in the cyclooctadiene ligand were calculated and included in the structure factor calculations but were not refined. The toluene molecule was disordered, and a two-site model was used to describe the disorder. All non-hydrogen atoms were refined anisotropically. Because it was not possible to unambiguously locate the toluene methyl carbon atom, neither it nor the toluene hydrogen atoms were included in the final refinement, which converged (largest shift = 0.01σ) with R = 0.026 and R_w = 0.041. The final difference Fourier showed no peaks greater than 0.7 e/Å^3 (toluene region). The values of the atomic scattering factors were taken from the usual tabulation,[17] and the effects of anomalous dispersion were included.[18]

Acknowledgment. We are grateful to the staff of the 3M Analytical and Properties Research Laboratory for the spectroscopic and analytical data and to Jim Westberg, who obtained the Raman spectra.

Registry No. **1**, 99594-08-8; **2**, 103835-65-0; **3**, 103835-66-1; **4**, 99594-10-2; **5**, 99594-03-3; **5**·C_6H_6, 103835-67-2; **6**, 99594-06-6; **7**, 99594-09-9; $(Ph_3P)_3Rh^+CH(SO_2CF_3)_2^-$, 88825-75-6; $[(C_8H_{12})RhCl]_2$, 12092-47-6; $[(C_8H_{12})IrCl]_2$, 12112-67-3.

Supplementary Material Available: Tables of general temperature factor expressions, bond angles, torsional angles, disordered toluene atomic coordinates, and calculated hydrogen atomic coordinates (6 pages); a listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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(14) The intensity data were processed as described in: *CAD 4 and SDP User's Manual*; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = (K/\mathrm{NPI})(C - 2B)$, where K = 20.1166 × (attenuation factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation is given by $\sigma^2(I) = (K/\mathrm{NPI})^2[C + 4B + (pI)^2]$ where p is a factor (here 0.04) used to downweight intense reflections.

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(16) All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD4/SDP program. This crystallographic computing package is described by Frenz (Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71). All least-squares refinements were based on the minimization of $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|)^2]^{1/2}$.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2A. Cromer, D. T. *Ibid.*; Table 2.3.1.

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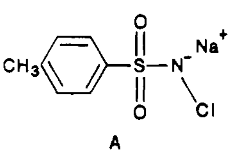
Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Crystal and Molecular Structure of Chloramine-T Trihydrate. Absence of a Sodium–Nitrogen Interaction in the Oxidant *N*-Chloro-*N*-sodiotoluene-*p*-sulfonamide

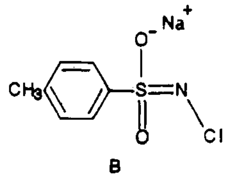
Marilyn M. Olmstead and Philip P. Power*

Received April 17, 1986

The wide variety of reactions undergone by chloramine-T (the sodium salt of *N*-chloro-4-methylbenzenesulfonamide) has attracted considerable interest. Two recent reviews,[1,2] however, have referred to the lack of structural data available for this and related compounds. The structure of chloramine-T is often represented as A or, much less commonly, B. These structures convey very different bonding descriptions. In A there is a single bond between sulfur and nitrogen and an interaction between the sodium ion and the nitrogen center. In B a sulfur–nitrogen double bond is inferred, as well as an interaction between the sodium ion and one or both oxygens. A survey of the literature does little to shed further light on a correct structural assignment. There are no X-ray structures for any $[RSO_2NCl]^-$ grouping although the structures of a number of sulfilimines $[RSO_2NR']^-$[3–5] are known. Crystal structures of nitrogen–halide-bonded compounds are also understandably rare.



A



B

In this paper we report the structure of $[Na][4\text{-}MeC_6H_4SO_2NCl]\cdot 3H_2O$, chloramine-T, and show by X-ray crystallography that there is no interaction between nitrogen and sodium. Instead the Na^+ ion interacts with one of the sulfonyl oxygens and a chlorine from a neighboring $[4\text{-}MeC_6H_4SO_2NCl]^-$ ion. The remainder of the roughly octahedral Na^+ coordination sphere involves oxygens from waters of crystallization. The structure is therefore closer to the formulation B than to its more common representation as A.

Crystal Data, X-ray Data Collection, and Solution and Refinement of Structure

The colorless crystals of chloramine-T (Aldrich) are readily obtained by slow evaporation of an aqueous or ethanolic solution of the compound. Those obtained from water grow as thin, frequently twinned plates; however, on the basis of cell dimensions, they are isomorphous with those obtained from ethanol. A parallelepiped of dimensions 0.12 × 0.32 × 0.60 mm from an ethanol recrystallization was selected for X-ray data collection. A Syntex P2$_1$ diffractometer equipped with a graphite monochromator was used. Crystal data (293 K): triclinic, a = 6.393 (1) Å, b = 7.510 (1) Å, c = 13.767 (2) Å, α = 85.33 (1)°, β = 83.92 (1)°, γ = 74.11 (1)°, V = 631.2 (2) Å^3, d_{calcd} = 1.48 g cm^{-3}, Z = 2, space group $P\bar{1}$, μ(Mo Kα) = 5.0 cm^{-1}, range of absorption correction factors 1.05–1.15. An absorption correction was applied.[6] A total of 2891 data were collected in the range of $0 < 2\theta \leq 55°$, with hkl ranges 0 to +8, −9 to +9, and −17 to +17, respectively, of which 2366 ($I > 2\theta(I)$) were used in the solution and refinement of the structure. The structure was solved by direct methods. The function minimized throughout refinement was $w(|F_o| - k|F_c|)^2$, with $w = 1/\sigma^2(F_o)$. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of all three H_2O molecules were allowed to refine as isotropic atoms. The phenyl ring hydrogens were refined by use of a riding model on the bonded carbon and free thermal parameters. The methyl hydrogens are subject to very large thermal motion and were included in the structure factor calculation at fixed positions obtained from a difference map and with free thermal parameters. At convergence, R = 0.039, R_w = 0.048, $w = 1/\sigma^2(F)$, and GOF = 1.04, for 176 parameters.[7] Atom coordinates, isotropic thermal parameters, bond distances, and bond angles are given in Tables I and II.

Results and Discussion

The crystal structure of chloramine-T is complex and cannot easily be described by the usual packing of molecular species. The

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(6) Program XABS by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ differences.

(7) Scattering factors and the correction for anomalous dispersion were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. Crystallographic programs used were those of SHELXTL, version 4, installed on a Data General Eclipse computer.

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Table I. Atom Coordinates ($\times 10^4$) and Thermal Parameters ($Å^2 \times 10^3$)

atom	*x*	*y*	*z*	U^a
Cl	1752 (1)	−636 (1)	7152 (1)	54 (1)
S	897 (1)	3140 (1)	7272 (1)	37 (1)
Na	2638 (1)	6562 (1)	5474 (1)	41 (1)
O(1)	−1426 (2)	3278 (3)	7322 (1)	47 (1)
O(2)	1575 (3)	4693 (3)	6795 (1)	57 (1)
O(3)	3650 (3)	4279 (2)	4227 (1)	44 (1)
O(4)	−1048 (2)	8062 (2)	5253 (1)	41 (1)
O(5)	3321 (3)	8568 (2)	4013 (1)	44 (1)
N	2370 (3)	1421 (3)	6695 (1)	42 (1)
C(1)	1561 (3)	2903 (3)	8498 (2)	38 (1)
C(2)	3513 (4)	3165 (5)	8714 (2)	69 (1)
C(3)	4009 (5)	2915 (6)	9681 (2)	82 (2)
C(4)	2634 (4)	2450 (4)	10434 (2)	58 (1)
C(5)	708 (5)	2226 (5)	10203 (2)	71 (1)
C(6)	171 (4)	2432 (5)	9238 (2)	61 (1)
C(7)	3205 (7)	2187 (7)	11492 (3)	94 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table II. Important Bond Distances (Å) and Angles (deg)

N–Cl	1.750 (2)	Na–O(4)	2.357 (2)
N–S	1.590 (2)	Na–O(3)	2.437 (2)
S–O(1)	1.455 (2)	Na–O(5)	2.487 (2)
S–O(2)	1.439 (2)	Na–Cl″	3.153 (1)
S–C(1)	1.767 (2)	O(1)···H(3a)′	2.11 (3)
Na–O(2)	2.365 (2)	O(1)···H(5a)′	2.16 (3)
Cl–N–S	110.9 (1)	O(1)–S–O(2)	116.1 (1)
N–S–C(1)	109.6 (1)	O(1)–S–C(1)	105.8 (1)
O(1)–S–C(1)	105.8 (1)	O(2)–S–C(1)	103.3 (1)
S–O(2)–Na	157.0 (1)	O(2)–S–N	103.6 (1)

entity shown in Figure 1 is the dominant motif and can be roughly described as an aquo-bridged sodium dimer (Na–O = 2.354 (2), 2.437 (2) Å). In addition to the bridging water molecules, the halves of the dimer are held together by a hydrogen bond between a coordinated water molecule and the amido nitrogen (depicted by dotted lines). The sixth coordination site on each sodium is occupied by the chlorine of a neighboring dimer, obtained by a unit translation along *b* (Na···Cl = 3.153 (1) Å).

A different dimer, related by inversion, provides additional hydrogen bonds to N, O(1), O(4), and O(3). Thus, each hydrogen belonging to a water molecule is involved in some type of hydrogen bonding, while each water oxygen, as well as the nitrogen atom, has two hydrogen-bonded contacts. In addition, O(1), a sulfonyl oxygen, has two hydrogen bonds, but O(2) has none, as it is involved in coordination to the sodium. The "N-sodio" interaction is clearly a misnomer, at least in the solid state. The closest N···Na distance is 4.095 (2) Å, and it involves the nitrogen bonded to the coordinated chlorine. Furthermore, the octahedral set of five oxygens and one chlorine surrounding each sodium precludes the close approach of a nitrogen atom.

The N–Cl distance of 1.750 (2) Å equals the mean N–Cl distance in $NCl_3(s)$[8] and is the same as one of the distances in $[PtCl(NH_3)_3(NCl_2)_2]Cl$ (1.75 (2), 1.66 (2) Å).[9] The S–O(1) and S–O(2) distances are 1.455 (2) and 1.439 (2) Å, which are well within the range of those reported for similar molecules. The slightly longer S–O(1) bond length is presumably due to hydrogen bonding to O(1) but not O(2). The octahedral geometry around sodium is fairly regular. The five Na–O bonds range from 2.354 (2) to 2.487 (2) Å, and the largest deviation from idealized octahedral angles is 103.5 (1)° for O(3)–Na–O(4). This geometry is comparable to that found in sodium acetylacetonate monohydrate.[10] The toluene group is quite normal, with mean ring C–C bonds of 1.377 (4) Å and an average deviation from the mean of 0.009 Å.

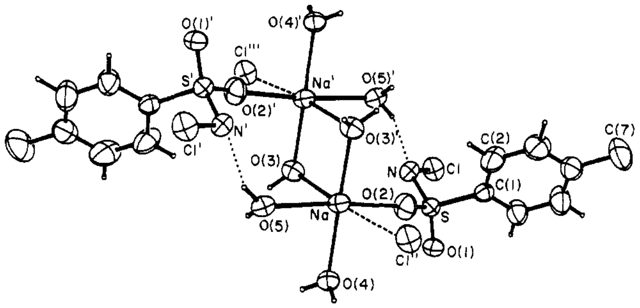

Figure 1. A computer-generated drawing of a portion of the structure of chloramine-T. Anisotropic thermal ellipsoids are shown at the 50% probability level. Centrosysmmetric dimers result from the bridging of sodium by water and from intradimer hydrogen bonds (dotted lines). In addition, the sixth coordination site on each sodium is filled by the chlorine of an adjacent dimer (dashed lines).

To our knowledge, the structure of the RSO_2NCl^- grouping is reported here for the first time. Support of formulation B for the structure of its sodium salt comes from three major structural features: (i) the only interaction between sodium and the SO_2N moiety involves an Na–O rather than an Na–N contact; (ii) the S–N distance, 1.590 (2) Å, is consistent with a double rather than a single bond;[11] (iii) aggregation is a result of the tendency of the Na^+ ion to achieve 6-coordination, which it does through coordination to one sulfonyl oxygen only; two bridging and two terminal waters and a chlorine from another chloramine-T molecule comprise the rest of the coordination sphere. This in turn gives rise to several hydrogen-bonding contacts between water hydrogens and oxygen and nitrogen atoms. Clearly then the aggregation seems to have no significant effect on the structure of the $[4\text{-}MeC_6H_4SO_2NCl]^-$ ion.

In summary, the best description of chloramine-T is that its structure is close to that depicted in B rather than its more common representation A.

Acknowledgment. We thank the Committee on Research of the University of California at Davis for financial support.

Registry No. Chloramine-T trihydrate, 7080-50-4.

Supplementary Material Available: Tables of bond distances and angles, hydrogen bonding interactions, hydrogen coordinates, and anisotropic thermal parameters (3 pages); a list of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Reversible Addition of CO to a Rh_3 Cluster: Synthesis and X-ray Crystal Structure of $Rh_3(\mu\text{-}t\text{-}Bu_2P)_3(\mu\text{-}CO)(CO)_4$

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Received May 1, 1986

Facile reversible addition of carbon monoxide to transition-metal clusters is an interesting phenomenon that is relevant to many homogeneous and heterogeneous catalytic reactions.[1] We report here the synthesis and X-ray crystal structure of $Rh_3(\mu\text{-}t\text{-}$

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(1) See for example: Farrugia, L. J.; Green, M.; Hankey, D. R.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 310-312. Schneider, J.; Minelli, M.; Huttner, G. *J. Organomet. Chem.* **1985**, *294*, 75-89 and references therein.

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