Inorganic Chemistry, Vol. 18, No. 9, 1979 **2427**

Contribution from the Department of Chemistry,
University of California, Berkeley, California 94720

Coordination Chemistry of Microbial Iron Transport Compounds. 18.[1] Crystal and Molecular Structure of Disodium Triethylmethylammonium Tris(thiobenzohydroximato)chromate(III) Hemikis(sodium hydroxide hydrate), $Na_2[(C_2H_5)_3(CH_3)N][Cr(PhC(S){=}N(O))_3]{\cdot}{}^1/_2NaH_3O_2{\cdot}18H_2O$

KAMAL ABU-DARI,[2] DEREK P. FREYBERG, and KENNETH N. RAYMOND*

Received January 26, 1979

The structure of the title compound, $Na_2[(C_2H_5)_3(CH_3)N][Cr(PhC(S){=}N(O))_3]{\cdot}{}^1/_2NaH_3O_2{\cdot}18H_2O$, has been determined by single-crystal X-ray diffraction methods using counter data. The structural parameters of the tris(thiobenzohydrox*i*mato)chromate(III) trianion are compared with those of the neutral tris(*N*-methylthiobenzohydrox*a*mato)chromium(III) as well as the square-planar *cis*- and *trans*-bis(thioacethydroxamato)nickel(II) in order to elucidate the mode of bonding in these thiohydrox*i*mato and thiohydrox*a*mato metal complexes. The average Cr–O and Cr–S bond lengths in the tris(thiobenzohydrox*i*mato)chromate(III) anion are 1.995 (6) and 2.379 (5) Å, which corresponds to a slight *increase* relative to those of the neutral tris(*N*-methylthiobenzohydrox*a*mato)chromium(III), 1.970 (3) and 2.307 (8) Å, respectively. The C–S and C–N bond distances in the chromium thiobenzohydrox*i*mato complex are only 0.03 Å longer and 0.02 Å shorter, respectively, than the corresponding bonds in the metal thiohydrox*a*mato complexes, implying that the modes of bonding are similar in both types of complexes; the thiohydroxamate ligand when coordinated exists predominantly in the form $RC(S^-){=}N^+(O^-)R'$. Both the tris(thiohydrox*i*mato)- and tris(thiohydrox*a*mato)chromium(III) complexes have identical trigonal twist angles of 48.7°. The first observation of the discrete $H_3O_2^-$ anion (a hydroxide hydrate) is reported. An unusually short hydrogen bond, 2.29 (2) Å, has been found for the $H_3O_2^-$ anion, which compares well with that of the isostructural bifluoride ion HF_2^-. Green crystals of the title compound, obtained from aqueous solutions of sodium hydroxide and triethylmethylammonium iodide, conform to space group $P\bar{1}$ with $a = 13.013$ (4) Å, $b = 13.204$ (4) Å, $c = 17.681$ (6) Å, $\alpha = 81.67$ (3)°, $\beta = 83.85$ (3)°, $\gamma = 59.76$ (2)°, $V = 2507$ (4) Å^3, $Z = 2$, $\rho_{calcd} = 1.353$ g cm^{-3}, and $\rho_{obsd} = 1.357$ (5) g cm^{-3}. The structure was solved by direct phasing methods followed by full-matrix least squares and Fourier techniques. In the final refinement, the 4136 independent data with $F^2 > 3\sigma(F^2)$ gave unweighted and weighted R factors of 6.08 and 6.32%, respectively.

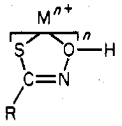
Introduction

The siderophores are low molecular weight compounds, whose manufacture by microbes, in order to facilitate the uptake of ferric iron, we have described in previous papers in this series.[3,4] The most common functional groups in the siderophores are the hydroxamate group, as in ferrichromes[5] and ferrioxamines,[6] and the catecholate group, as in enterobactin.[7] A new type of chelate moiety for the siderophore class of compounds came with the discovery that cupric and ferric complexes of *N*-methylthioformhydroxamic acid could be isolated from culture broths of *Pseudomonas fluorescens* grown on *n*-paraffin or sucrose as the only source of carbon.[8-14] These metal chelates, as well as the uncomplexed thioformhydroxamic acid, show antibiotic activity against certain microorganisms.[8-17]

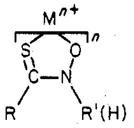
The ionic radii of high-spin ferric ion and chromic ion differ by only 0.03 Å,[18] so the geometries of the chromic complexes are of interest both to characterize the coordination sites of the siderophore complexes and to determine the degree to which chromic complexes mimic the naturally occurring ferric siderophores. We have recently reviewed this chemistry and the use of these kinetically inert complexes as biological probes in studies of microbial iron transport.[3]

Thiohydroxamic acids form coordination compounds with transition metals via their sulfur and oxygen atoms, with the loss of one proton. Two possible modes of coordination have been suggested for the transition-metal complexes with N-unsubstituted thiohydroxamic acids, as shown in structures Ia[19,20] and Ib.[21] Only structure Ib is possible for N-substituted thiohydroxamic acids. Neutral transition-metal complexes with N-unsubstituted thiohydroxamic acids dissolve in excess base with the loss of the second proton to form the anionic thiohydroximato complexes, with structure Id as the most plausible coordination mode for such complexes.

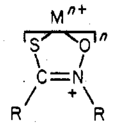
We have previously[22] reported the preparation of the tris(thiohydrox*a*mato) and -(thiohydrox*i*mato) complexes of chromium(III), iron(III) and cobalt(III), as well as the resolution of the tris(thiohydroxamato) complexes (via the resolution of the corresponding thiohydroximato complexes, followed by protonation and extraction of the neutral thiohydroxamato chelates). We assigned a cis geometry to these complexes on the basis of their physical properties and their circular dichroism spectra. Following this we have reported the crystal and molecular structures of tris(*N*-methylthiobenzohydroxamato)iron(III), -chromium(III), -cobalt(III), and -manganese(III).[1] Murray et al. have reported the crystal and molecular structure of the ferric complex of *N*-methylthioformhydroxamic acid[23] and Leong and Bell have reported the separation of the geometrical isomers of chromium(III), rhodium(III), and platinum(III) complexes with *N*-methylthioformhydroxamic acid.[24]



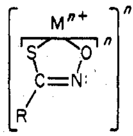
Ia



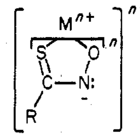
Ib



Ic



Id



Ie

We report here the crystal and molecular structure of the title compound, $Na_2[(C_2H_5)_3(CH_3)N][Cr(C_6H_5C(S){=}N(O))_3]{\cdot}{}^1/_2NaH_3O_2{\cdot}18H_2O$, which is the first structure of a thiohydroximato–metal complex to be determined. Comparison of the modes of binding in thiohydroxamato– and thiohydroximato–metal complexes and the observation of a distinct $H_3O_2^-$ ion with a very short hydrogen bond are the salient features of the discussion.

Experimental Section

Materials. Sodium thiobenzohydroxamate was prepared as described elsewhere.[25] The tetrahydrofuran adduct of chromic chloride,

© 1979 American Chemical Society

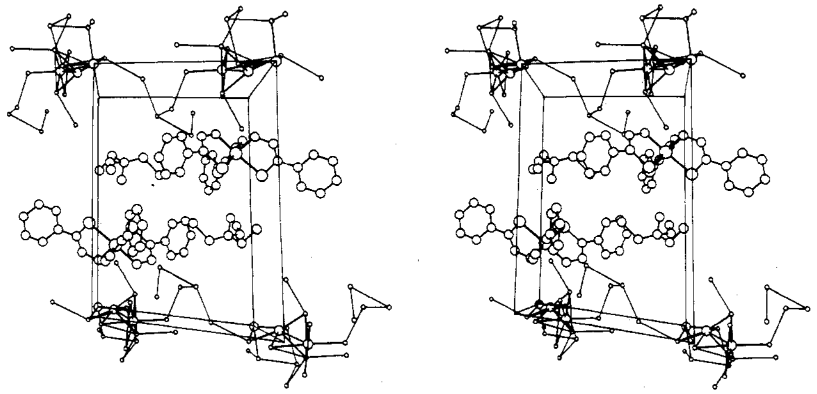


Figure 1. A stereoscopic packing diagram of the compound $Na_2[(C_2H_5)_3(CH_3)N][Cr(PhC(S){=}N(O))_3]\cdot{}^1/_2NaH_3O_2\cdot 18H_2O$. The structure is viewed down the crystallographic *a* axis. The vertical axis is *c*. The atoms in the *C* face are the sodium ions (large circles) and water oxygen atoms (small circles); the oxygen atoms are connected with hydrogen bonds ~3.1 Å in length.

$CrCl_3\cdot 3THF$, was prepared by a literature method[26] and protected from moisture. Tris(thiobenzohydroxamato)chromium(III) was prepared as described earlier.[22]

Microanalyses. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, University of California, Berkeley, Calif.

Synthesis of $Na_2[(C_2H_5)_3(CH_3)N][Cr(C_6H_5C(S){=}N(O))_3]\cdot{}^1/_2NaH_3O_2\cdot 18H_2O$. Tris(thiobenzohydroxamato)chromium(III) (12 g, 0.0228 mol) was dissolved in 120 mL of an aqueous solution of sodium hydroxide (15 g, 0.375 mol) at room temperature. The solution was heated slowly under nitrogen to about 90 °C, and 30 mL of a concentrated aqueous solution of triethylmethylammonium iodide (12 g, 0.049 mol) was added. The resultant solution was filtered and allowed to cool slowly to room temperature. Large green crystals were usually obtained within 48 h.

The compound loses some of its water of hydration in air; hence crystals suitable for data collection were mounted in glass capillaries with a small amount of the mother liquor and sealed. Densities were measured for fresh crystals by flotation in iodobutane/heptane mixtures.

Analyses for the fully hydrated crystals were not possible due to their tendency to lose water. Drying a sample in air overnight gave the following analysis. Anal. Calcd for $Na_2(C_7H_{18}N)[Cr(C_7H_5NOS)_3]\cdot{}^1/_2NaH_3O_2\cdot 11H_2O$: C, 37.82; H, 6.40; N, 6.30; S, 10.79. Found: C, 37.8; H, 5.5; N, 6.3; S, 10.1. After drying under high vacuum at room temperature for 12 h, the dried sample gave the following analysis. Anal. Calcd for $Na_2(C_7H_{18}N)[Cr(C_7H_5NOS)_3]\cdot{}^1/_2NaH_3O_2\cdot 2H_2O$: C, 46.24; H, 5.34; N, 7.70; S, 13.20; Na, 7.91. Found: C, 45.74; H, 5.05; N, 7.67; S, 12.98; Na, 7.92.

In order to establish the formulation as a hemihydroxide double salt, we dissolved the dried crystals in water and potentiometrically titrated the solution with standard HCl solution. The first break in the pH–volume plot occurred at pH 9.7, which corresponds to the end point of the hydroxide content. The equivalent weight was 1.47×10^3 (calcd) and 1.46×10^3 (found).

Unit Cell and Diffraction Data. Preliminary cell dimensions were obtained by using the program SEARCH[27] to obtain the positions of 25 reflections. Crystal data, obtained by a least-squares fit to the setting angles of 22 high-angle, accurately centered reflections, are given in Table I. The crystal data and the lack of any systematic absences imply the triclinic space groups $P1$ or $P\bar{1}$. The latter is confirmed by the final structure.

Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer controlled by a PDP-8/E computer, using monochromatic Mo Kα radiation.[28] The 9486 data were reduced to F^2 and $\sigma(F^2)$ as previously described[29,30] and averaged to give 4234 independent reflections with $F^2 > 3\sigma(F^2)$. The *R* factor for averaging was 2.1% on F^2. The parameter *p*, introduced to prevent overweighting of the strong reflections,[29] was set to 0.03. Lorentz and polarization corrections were applied, but correction for absorption was considered unnecessary (μ = 4.59 cm^{-1}).

Solution and Refinement of the Structure. The positions of the chromium and the thiohydroximate ring atoms were obtained with MULTAN[27] by using the 300 highest *E* values. This led to the location of all the nonhydrogen atoms by standard difference Fourier and least-squares techniques.[31-34] Examination of the Fourier map showed that the triethylmethylammonium cation is disordered, especially the methylene carbons; with several peaks in the region in which these carbon atoms are expected, only the main peaks were refined. The phenyl rings were introduced in the final refinement as rigid groups (C–C bond distance = 1.395 Å and C–C–C angles = 120.0°[35]), with isotropic refinement of the carbon atoms. The phenyl hydrogen atoms were located from the difference Fourier map and were found to correspond to the calculated positions. Phenyl hydrogens and a few water hydrogens were introduced as fixed contributions to *F*. Final full-matrix least-squares refinement with 422 variables and with use of the 4136 reflections with $F^2 > 3\sigma(F^2)$ led to convergence with R = 6.08% and R_w = 6.32% and the error in an observation of unit weight = 1.94%. The relatively high *R* factors and goodness of fit are ascribed to the alkylammonium cation disorder.

Table I. Summary of Crystal Data for $Na_2[(C_2H_5)_3(CH_3)N][Cr(C_6H_5C(S){=}N(O))_3]\cdot{}^1/_2NaH_3O_2\cdot 18H_2O$

formula wt	1021.05
space group	$P\bar{1}$
cell constants[a]	
a, Å	13.013 (4)
b, Å	13.204 (4)
c, Å	17.081 (6)
α, deg	81.67 (3)
β, deg	83.85 (3)
γ, deg	59.76 (2)
cell volume, Å^3	2507 (4)
formula units/cell, *Z*	2
calcd density, g cm^{-3}	1.353
obsd density, g cm^{-3}	1.357 (5)
cryst dimensions, mm	0.30 × 0.27 × 0.15
absorption coeff ($\mu_{\text{Mo K}\alpha}$), cm^{-1}	4.59

[a] Ambient temperature of 23 °C; Mo Kα_1 radiation, λ = 0.70926 Å.

Table II gives the positional and thermal parameters of the nonhydrogen atoms. Root-mean-square amplitudes of vibrations for the nonhydrogen atoms are given in Table III.[36]

Description of the Structure

The crystal structure consists of tris(thiobenzohydroximato)chromate(III) anions, hydrated sodium cations, the $H_3O_2^-$ anion, and waters of crystallization, which are all linked by hydrogen bonds. The central region of the unit cell (Figure 1) contains the symmetry-related chromium complex anions and the triethylmethylammonium cations so oriented that they form a hydrophobic layer in the *ab* plane at $z = {}^1/_2$ that extends through the structure. The hydrophilic N–O groups point outward toward the *C* faces of the unit cell where the sodium ions, the $H_3O_2^-$ anion, and the waters of crystallization form hydrophilic layers that interleave the hydrophobic sheets.

A perspective view of the structure of the tris(thiobenzohydroximato)chromate(III) anion, with the numbering scheme, is shown in Figure 2. The chelate rings are arranged in the cis geometry, with the chromium atom lying on an approximate threefold axis and coordinated by three sulfur and three

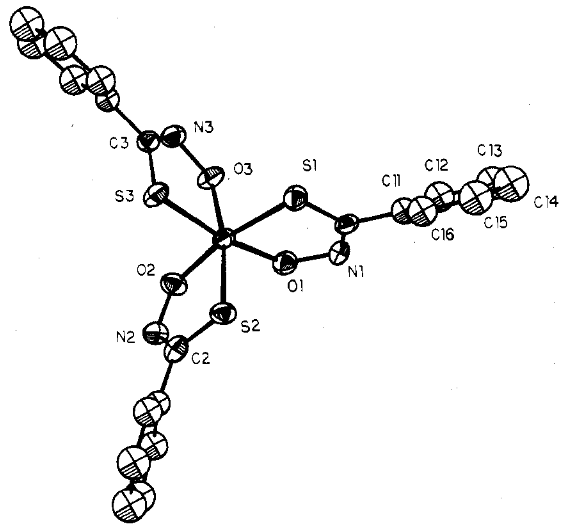


Figure 2. A perspective drawing of the $[Cr(PhC(S){=}N(O))_3]^{3-}$ anion, as viewed down the molecular threefold axis.

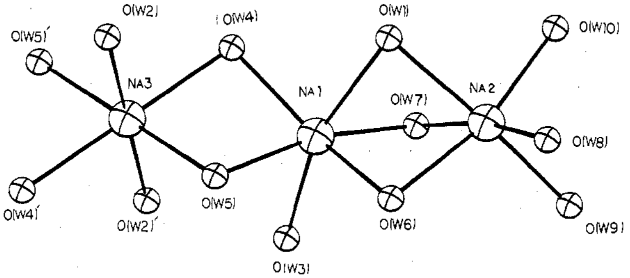


Figure 3. A perspective drawing of the coordination about the sodium ions.

oxygen atoms. Bond lengths and angles involving the thiohydroximato–metal complex are given in Table IV. The thiohydroximate rings are nearly planar and bend away from the Cr atoms such that the average Cr-to-plane distance is 0.11 (2) Å (Table V).[36]

Each sodium ion is coordinated in an approximately octahedral array to six water molecules, with Na(1) and Na(2) ions bridged by water molecules 1, 6, and 7. Sodium ion 3 lies at the cell origin ($\bar{1}$ symmetry) and is bridged to Na(1) by water molecules 4 and 5, forming a chain of water-bridged sodium ions as shown in Figure 3. Bond lengths and angles of the coordination of the sodium ions are given in Table VIa,b,[36] respectively.

Oxygen atom W(16) lies near an inversion center (0, $^1/_2$, 0) and is only 2.29 (2) Å from its inversion-related atom. This distance corresponds to a very short hydrogen bond—too short for a water–water interaction. This and the stoichiometry of the missing half-hydroxide lead us to assign this as the previously unobserved $H_3O_2^-$ anion, composed of a central proton on or near the inversion center (this is not clear from the Fourier maps) surrounded by two OH^- groups. The $H_3O_2^-$ anion is then itself linked to the extensive hydrogen bond system of the waters of crystallization as shown in Figure 4. The moderately high thermal motion of W(16) may be an artifact of some slight disorder about the inversion center, but even the extreme correction for thermal motion, assuming an independent movement[37] of both oxygen atoms, still gives an O–O bond of 2.377 (12) Å. In addition to the bond distances and angles shown in Figure 4, other hydrogen bond interactions are summarized in Table VII.

Discussion

The Tris(thiobenzohydroximato)chromate(III) Anion. The disodium triethylmethylammonium salt of tris(thiobenzohydroximato)chromate(III) is the first metal–thiohydroximate complex whose structure has been determined by X-ray diffraction. (We have previously investigated the structure of the tripotassium salt of tris(thiobenzohydroximato)chromate(III) but disorder in one of the potassium ions has so far prevented further refinement of the structure.) As shown in Figures 2 and 5, the tris(thiohydroximato)chromate(III) anion has approximate C_3 point group symmetry, with average Cr–S and Cr–O bond distances of 2.379 (5) and 1.995 (6) Å, respectively. The trigonal face containing the three sulfur atoms is parallel to that containing the three oxygen atoms (dihedral angle = 0.6°). The planarity of the chelate rings can be seen in the least-squares planes through the S, C, N, and O atoms, Table V. Each of the five-membered thiohydroximate–metal rings is in an envelope conformation in which the metal is bent up an average of 0.11 (2) Å from the planar chelate ring. Rings 1 and 2 bend in one direction around the trigonal axis and ring 3 bends the opposite direction.[36] The calculated trigonal twist angle (48.7°) compares well with that of tris(*N*-methylthiobenzohydroxamato)chromium(III) (48.7°)[1] and suggests that there is no major change in the distribution of

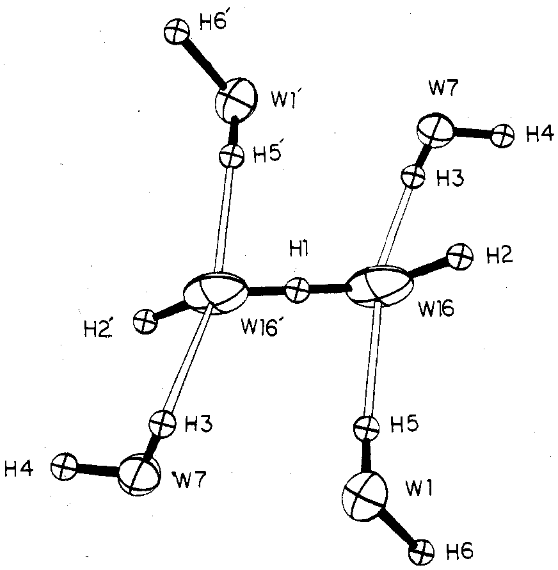


Figure 4. A perspective view of the structure of the $H_3O_2^-$ anion and the weak hydrogen bonding formed between it and adjacent waters of crystallization. Hydrogen atoms 2, 3, 4, and 6 have been located from the difference Fourier. Hydrogen atoms 1 and 5 were not seen in the electron density maps. Their positions are deduced from those of the other atoms in the structure.

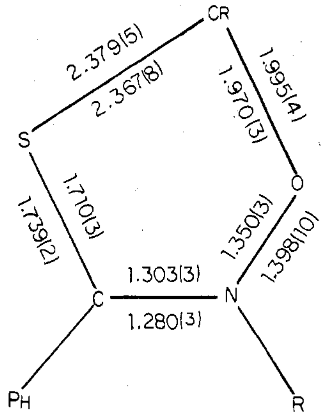


Figure 5. A comparison of the average bond lengths of the chelate rings in the neutral tris(*N*-methylthiobenzohydroxamato)chromium(III) (R = CH_3, bond lengths inside the chelate ring) and tris(thiobenzohydroximato)chromate(III) trianion (R = electron pair, bond lengths outside the chelate ring).

Table II

(a) Positional and Thermal Parameters ($\times10^3$) for the Nonhydrogen Atoms in $Na_2[(C_2H_5)_3(CH_3)N][Cr(thiobenz(-H))_3]\cdot{}^1/_2NaH_3O_2\cdot18H_2O$

atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.34202 (9)	0.87077 (9)	0.28506 (6)	3.23 (10)	4.23 (10)	2.13 (5)	−2.12 (8)	−0.15 (5)	−0.23 (5)
S_1	0.51232 (15)	0.76824 (16)	0.36366 (10)	3.97 (16)	5.93 (17)	2.30 (7)	−2.01 (14)	−0.41 (9)	−0.92 (9)
S_2	0.24913 (16)	0.77199 (16)	0.36190 (10)	4.90 (17)	6.55 (18)	2.49 (8)	−3.89 (15)	−0.94 (9)	0.66 (9)
S_3	0.25363 (16)	1.03028 (16)	0.36543 (10)	5.67 (18)	5.73 (17)	2.17 (7)	−3.33 (15)	0.81 (9)	−0.84 (9)
Na_1	0.1987 (3)	0.1124 (3)	−0.00537 (18)	8.3 (3)	11.1 (3)	3.75 (14)	−6.3 (3)	−0.51 (17)	−0.03 (17)
Na_2	0.3501 (3)	0.2381 (3)	0.0264 (2)	10.4 (4)	12.1 (4)	5.47 (17)	−6.5 (3)	−0.5 (2)	−0.9 (2)
Na_3	0.0	0.0	0.0	7.4 (4)	9.3 (4)	3.51 (18)	−5.4 (4)	−0.4 (2)	−0.6 (2)
O_1	0.4422 (4)	0.7432 (4)	0.2157 (2)	4.6 (4)	4.1 (4)	2.56 (19)	−1.3 (4)	−0.6 (2)	−0.4 (2)
O_2	0.2039 (4)	0.9296 (4)	0.2159 (2)	4.5 (4)	6.5 (4)	2.19 (19)	−3.6 (4)	−0.7 (2)	0.7 (2)
O_3	0.3916 (4)	0.9760 (4)	0.2176 (2)	4.9 (4)	5.5 (4)	2.45 (19)	−3.3 (4)	0.5 (2)	−0.8 (2)
O(W1)	0.1598 (6)	0.2611 (6)	0.0905 (3)	11.2 (7)	14.3 (7)	5.0 (3)	−7.0 (6)	−0.2 (4)	−0.3 (4)
O(W2)	−0.0835 (4)	0.0312 (4)	0.1367 (3)	6.7 (5)	9.5 (5)	3.5 (2)	−5.4 (4)	−0.6 (3)	0.2 (3)
O(W3)	0.2756 (5)	0.0009 (5)	−0.1205 (3)	8.4 (6)	10.8 (6)	3.9 (2)	−6.7 (5)	−0.1 (3)	−0.1 (3)
O(W4)	−0.0134 (5)	0.1929 (5)	−0.0088 (3)	8.6 (6)	8.9 (5)	4.4 (3)	−4.2 (5)	−1.0 (3)	−0.3 (3)
O(W5)	0.1888 (5)	−0.0590 (5)	0.0549 (3)	7.2 (5)	10.2 (6)	3.7 (2)	−4.7 (5)	−0.4 (3)	0.0 (3)
O(W6)	0.3862 (5)	0.0327 (5)	0.0553 (3)	9.7 (6)	10.1 (6)	3.8 (2)	−5.9 (5)	−0.9 (3)	−0.2 (3)
O(W7)	0.2423 (5)	0.2508 (5)	−0.0857 (3)	12.9 (7)	9.5 (6)	4.4 (3)	−6.7 (6)	−0.6 (3)	−0.6 (3)
O(W8)	0.4775 (5)	0.1893 (5)	0.1371 (3)	11.1 (6)	9.3 (6)	4.2 (3)	−6.7 (5)	0.2 (3)	−0.2 (3)
O(W9)	0.5160 (6)	0.2186 (5)	−0.0552 (3)	12.7 (7)	11.5 (7)	4.2 (3)	−4.4 (6)	0.8 (4)	0.3 (3)
O(W10)	0.2644 (7)	0.4489 (6)	0.0063 (5)	18.4 (10)	12.1 (8)	9.6 (5)	−6.4 (7)	1.5 (5)	−3.7 (5)
O(W11)	0.6318 (5)	0.8690 (5)	0.2129 (3)	6.9 (5)	9.3 (6)	5.2 (3)	−4.5 (5)	0.9 (3)	0.5 (3)
O(W12)	0.0740 (5)	0.1639 (5)	0.2185 (3)	8.1 (6)	8.6 (6)	5.0 (3)	−2.7 (5)	−1.0 (3)	−0.9 (3)
O(W13)	−0.1312 (5)	0.2636 (5)	0.1393 (3)	9.7 (6)	10.1 (6)	5.5 (3)	−3.8 (5)	−1.3 (3)	−2.7 (3)
O(W14)	0.3409 (5)	0.6059 (5)	0.2126 (4)	11.7 (7)	11.0 (6)	7.3 (3)	−7.3 (6)	0.3 (4)	−3.3 (4)
O(W15)	0.3459 (5)	0.5287 (5)	−0.1382 (4)	9.6 (7)	10.8 (6)	6.2 (3)	−2.8 (5)	0.5 (4)	−5.0 (4)
O(W16)	−0.0195 (6)	0.5183 (6)	0.0651 (5)	10.0 (8)	10.3 (7)	11.4 (5)	1.2 (6)	0.6 (5)	1.2 (5)
O(W17)	0.5124 (7)	0.6102 (6)	−0.1489 (5)	14.2 (9)	13.7 (8)	13.7 (6)	−9.3 (7)	2.9 (6)	−5.5 (6)
O(W18)	0.1967 (9)	0.6284 (8)	0.0988 (5)	29.9 (16)	18.5 (11)	9.2 (5)	1.1 (11)	−9.6 (8)	−3.8 (6)
O(W19)	0.3503 (12)	0.7085 (12)	−0.0096 (6)	39 (2)	49 (2)	12.1 (7)	−35.0 (2)	6.4 (9)	−11.1 (11)
N_1	0.5530 (5)	0.6499 (5)	0.2377 (4)	4.1 (5)	4.0 (5)	3.6 (3)	−1.7 (4)	−0.7 (3)	0.0 (3)
N_2	0.1132 (5)	0.9000 (5)	0.2376 (3)	3.8 (5)	5.4 (5)	2.9 (2)	−2.8 (4)	−0.7 (3)	0.0 (3)
N_3	0.3693 (5)	1.0814 (5)	0.2415 (4)	4.9 (6)	5.0 (5)	3.5 (3)	−3.0 (5)	0.2 (3)	−0.6 (3)
$N(R_4N)$	0.6792 (7)	0.1816 (8)	0.3720 (5)	9.3 (8)	13.7 (9)	3.8 (3)	−6.0 (8)	−0.4 (4)	−0.4 (5)
C_1	0.5895 (6)	0.6556 (6)	0.3031 (4)	4.7 (6)	5.2 (6)	2.2 (3)	−3.0 (5)	−0.4 (3)	0.2 (3)
C_2	0.1278 (6)	0.8318 (6)	0.3017 (4)	3.7 (6)	4.3 (6)	2.1 (3)	−2.1 (5)	−0.6 (3)	0.2 (3)
C_3	0.3081 (6)	1.1129 (6)	0.3059 (4)	3.3 (6)	5.4 (6)	2.4 (3)	−2.2 (5)	0.3 (3)	−0.7 (3)
$C_1(R_4N)$	0.8908 (18)	0.1038 (17)	0.4208 (14)	20 (2)	22 (2)	16.5 (15)	−5.2 (18)	−7.7 (16)	−3.6 (14)
$C_2(R_4N)$	0.6034 (14)	0.0295 (13)	0.4021 (10)	21 (2)	19.7 (18)	14.4 (11)	−13.6 (16)	−4.4 (12)	−0.6 (11)
$C_3(R_4N)$	0.5293 (16)	0.3965 (15)	0.4050 (12)	23 (2)	21 (2)	16.8 (13)	−13.1 (19)	7.7 (14)	−7.8 (14)
$C_4(R_4N)$	0.629 (4)	0.108 (5)	0.374 (3)	92 (12)	110 (14)	41 (6)	−85 (12)	4 (6)	−31 (7)
$C_5(R_4N)$	0.655 (5)	0.289 (4)	0.329 (4)	85 (13)	58 (8)	46 (7)	−51 (9)	−36 (8)	32 (7)
$C_6(R_4N)$	0.795 (6)	0.126 (5)	0.346 (4)	81 (13)	80 (11)	57 (7)	−50 (11)	56 (9)	−52 (8)
$C_7(R_4N)$	0.716 (4)	0.146 (4)	0.4437 (13)	106 (11)	90 (9)	5.8 (11)	−52 (9)	−14 (3)	4 (2)

(b) Derived Positional and Thermal Parameters for the Phenyl Carbon Atoms

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C_{11}	0.7114 (3)	0.5572 (4)	0.3251 (3)	2.61 (13)	C_{24}	−0.1279 (4)	0.7172 (5)	0.3608 (3)	5.7 (2)
C_{12}	0.7344 (4)	0.5097 (4)	0.4039 (2)	3.83 (16)	C_{25}	−0.0911 (5)	0.7293 (5)	0.2819 (3)	4.80 (19)
C_{13}	0.8490 (5)	0.4220 (5)	0.4247 (2)	5.3 (2)	C_{26}	−0.0089 (4)	0.7682 (4)	0.2624 (2)	3.62 (15)
C_{14}	0.9406 (4)	0.3816 (4)	0.3668 (3)	5.8 (2)	C_{31}	0.2784 (4)	1.2294 (3)	0.3281 (3)	2.81 (14)
C_{15}	0.9176 (4)	0.4291 (5)	0.2880 (3)	4.97 (19)	C_{32}	0.2815 (5)	1.2439 (4)	0.4070 (2)	3.94 (17)
C_{16}	0.8031 (4)	0.5168 (4)	0.2672 (2)	3.51 (15)	C_{33}	0.2511 (5)	1.3542 (5)	0.4279 (2)	5.3 (2)
C_{21}	0.0365 (4)	0.7951 (4)	0.3217 (3)	2.40 (13)	C_{34}	0.2176 (6)	1.4501 (5)	0.3700 (3)	6.1 (2)
C_{22}	−0.0003 (5)	0.7830 (5)	0.4006 (2)	3.86 (16)	C_{35}	0.2145 (5)	1.4356 (4)	0.2911 (3)	4.92 (19)
C_{23}	−0.0825 (5)	0.7441 (5)	0.4201 (2)	4.90 (19)	C_{36}	0.2449 (5)	1.3253 (4)	0.2702 (2)	3.64 (16)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Bond Distances (Å) and Angles (deg) for the [Cr(thiobenzohydroximato)$_3$]$^{3-}$ Anion[a]

bond or angle[b]	ring 1	ring 2	ring 3	av[c]
Cr-S	2.374 (2)	2.374 (3)	2.388 (2)	2.379 (5)
Cr-O	1.994 (4)	2.003 (5)	1.988 (6)	1.995 (6)
C-S	1.735 (7)	1.742 (7)	1.741 (8)	1.739 (8)
N-O	1.390 (6)	1.418 (9)	1.387 (9)	1.398 (10)
C-N	1.285 (10)	1.278 (8)	1.276 (9)	1.280 (10)
C-C(Ph)	1.502 (7)	1.486 (10)	1.482 (9)	1.490 (9)
S-Cr-O	82.5 (1)	82.9 (2)	82.2 (1)	82.5 (2)
Cr-S-C	94.4 (2)	94.7 (3)	94.7 (2)	94.6 (3)
Cr-O-N	121.9 (4)	120.9 (3)	121.4 (4)	121.4 (4)
S-C-N	125.4 (4)	125.5 (7)	123.8 (7)	124.9 (7)
S-C-C(Ph)	119.2 (5)	118.6 (4)	119.2 (4)	119.0 (5)
N-C-C(Ph)	115.4 (5)	115.7 (6)	116.9 (7)	116.0 (7)
O-N-C	115.5 (5)	115.9 (6)	117.5 (7)	116.3 (7)
S(*i*)-Cr-S(*i* + 1)[d]	91.58 (8)	92.83 (8)	91.23 (8)	91.9 (8)
O(*i*)-Cr-O(*i* + 1)[d]	90.0 (2)	89.3 (2)	89.5 (2)	89.6 (2)
S(*i*)-Cr-O(*i* + 1)[d]	170.1 (2)	170.2 (1)	169.0 (2)	169.8 (4)
O(*i*)-Cr-S(*i* + 1)[d]	96.4 (2)	97.2 (1)	97.0 (2)	96.9 (2)

[a] Phenyl carbon atoms were refined as rigid groups; see text. [b] Atom numbers correspond to those in Figure 2. [c] Averages are computed as $\bar{x} = (1/n)\Sigma x_i$ and $\sigma^2(\bar{x}) = [1/n(n-1)][\Sigma(x_i - \bar{x})^2]$. [d] Modulo 3.

Table VI[a]

(a) Bond Distances (Å) for the Na(H$_2$O)$_6$$^+$ Ions

Na(1)-O(w1)	2.558 (8)	Na(2)-O(w7)	2.432 (8)
Na(1)-O(w3)	2.444 (6)	Na(2)-O(w8)	2.445 (7)
Na(1)-O(w4)	2.411 (7)	Na(2)-O(w9)	2.361 (8)
Na(1)-O(w5)	2.405 (8)	Na(2)-O(w10)	2.405 (8)
Na(1)-O(w6)	2.403 (7)	Na(3)-O(w2)	2.467 (5)
Na(1)-O(w7)	2.387 (7)	Na(3)-O(w4)	2.447 (7)
Na(2)-O(w1)	2.486 (8)	Na(3)-O(w5)	2.425 (5)
Na(2)-O(w6)	2.489 (8)		

[a] Table VIb is given in the supplementary material.

Table VII. Hydrogen Bond Interactions (within 3.1 Å)

O(w1)-O(w6)	3.054 (7)	O(w8)-N(3)	2.818 (10)
O(w1)-O(w7)	3.083 (8)	O(w9)-O(w19)	2.75 (2)
O(w1)-O(w12)	2.790 (9)	O(w9)-O(1)	2.760 (7)
O(w1)-O(w16)	2.996 (8)	O(w10)-O(w15)	2.853 (11)
O(w2)-O(w3)	2.784 (10)	O(w10)-O(w18)	2.752 (13)
O(w2)-O(w13)	2.815 (9)	O(w11)-O(w3)	2.703 (7)
O(w2)-N(2)	2.853 (7)	O(w12)-O(w13)	2.721 (8)
O(w3)-O(w8)	2.931 (7)	O(w12)-O(2)	2.681 (7)
O(w3)-O(w11)	2.791 (9)	O(w13)-O(w15)	2.758 (7)
O(w4)-O(w13)	2.835 (8)	O(w14)-O(w17)	2.816 (10)
O(w4)-O(w18)	2.772 (10)	O(w14)-O(w18)	2.727 (14)
O(w5)-O(w19)	3.007 (14)	O(w14)-O(1)	2.735 (11)
O(w5)-O(2)	2.755 (7)	O(w15)-O(w17)	2.844 (13)
O(w6)-O(w9)	2.894 (9)	O(w15)-N(1)	2.782 (9)
O(w6)-O(3)	2.763 (7)	O(w16)-O(w16)	2.294 (12)
O(w7)-O(w11)	2.743 (8)	O(w17)-O(w19)	2.976 (14)
O(w7)-O(w16)	3.002 (8)	O(w18)-O(w19)	3.05 (2)
O(w8)-O(w17)	2.753 (12)		

the electron density around the chromium ion (see below).

The torsional angles between the thiohydroximate chelate rings and the phenyl rings are about the same for the three thiohydroximate molecules, 41.7 (1)°. An investigation of the dependence of bond lengths on torsional angles has determined, by extrapolation to a torsional angle of 90°, that a pure sp^2–sp^2 carbon–carbon single bond should have a bond distance of 1.513 Å.[38] The bond distances in the present structure are 1.48–1.50 Å; for the tris(*N*-methylthiobenzohydroxamato)chromium(III), with torsional angles of 45.8–67.1°,[1] the average C–C bond length is 1.48 (1) Å. This bond distance is also 1.48 (1) Å for tris(benzohydroxamato)chromium(III), with torsional angles in the range 1.2–13.4°,[30] indicating the rotation occurs freely about this C–C bond and that the orientation of the phenyl groups in such compounds is determined solely by packing forces and does not affect the C–C bond length.

One of the main objects of the determination of the current structure is to examine the different modes of bonding suggested for the thiohydroxamate complexes, as shown in structures Ia–d. An explicit comparison is made in Figure 5 of the chelate ring bond parameters for the neutral and trianionic complexes. In Table VIII are given the averages of some of the bond distances and angles for the present structure along with those of tris(*N*-methylthiobenzohydroxamato)chromium(III),[1] the square-planar *cis*- and *trans*-bis(thioacethydroxamato)nickel(II),[39–42] and *trans*-tris(benzohydroxamato)chromium(III).[30] Examination of the modes of bonding suggested for the thiohydroxamate complexes, structures Ia,b, shows that the C–N and C–S bond distances and the C–N–O and S–C–N bond angles should be diagnostic parameters in choosing the dominant mode of bonding. As shown in Figure 5 and Table VIII, the C–S and C–N bond distances in the chromium thiobenzohydroximato complex are only 0.03 Å longer and 0.02 Å shorter, respectively, than in the thiohydroxamate structures; furthermore, the C–N bond distance in both the thiohydroxamato and thiohydroximato complexes is significantly shorter than the normal C–N single bond (1.43–1.45 Å[42]) and is only slightly longer than the C═N double bond in *O*-ethylbenzohydroximic acid (1.27 Å[43]), while the C–S bond distances show significant double bond character. The C–N–O and S–C–N angles are within 5° of the sp^2 hybridization angle of 120°, and the N–O bond distance increases by 0.05 Å upon deprotonation. These bond distances and angles and their changes upon deprotonation are consistent with resonance structures Ic for the thiohydroxamato and Id for the thiohydroximato complexes. This suggestion is supported by the location of the N–H hydrogen in the tris(benzohydroxamato)chromium(III) and by the fact that the C–S and C–N bond distances are rather close to those of a C–S single bond and C–N double bond, respectively.

Hydrogen Bonding and the H$_3$O$_2$$^-$ Ion. Hydrogen bonds between water molecules and between water molecules and

Table VIII. A Comparison of Structural Parameters for Thiohydrox*i*mato, Thiohydrox*a*mato, and Hydroxamato Complexes

bond distnace (Å) or angle (deg)	Cr(thiobenzohydroximate)$_3$$^{3-}$ [a]	Cr(*N*-methylthiobenzohydroxamate)$_3$ [b]	*cis*-Ni(thioacethydroxamate)$_2$ [c]	*trans*-Ni(thioacethydroxamate)$_2$ [d]	*trans*-Cr(benzohydroxamate)$_3$ [e]
Cr-S	2.379 (5)	2.367 (8)			
Cr-O	1.995 (6)	1.970 (3)			1.984 (7)
C-S	1.739 (8)	1.710 (3)	1.730 (10)	1.710 (10)	
C-N	1.280 (10)	1.303 (3)	1.290 (13)	1.300 (13)	1.307 (5)
N-O	1.398 (10)	1.350 (3)	1.35 (2)	1.370 (10)	1.374 (5)
C-C	1.490 (9)	1.484 (4)	1.51 (2)	1.51 (2)	1.484 (3)
S-C-N	124.9 (7)	120.0 (2)	117.0 (8)	118.8 (8)	
C-N-O	116.3 (7)	121.0 (2)	122.5 (5)	121.6 (8)	
O-Cr-S	82.5 (2)	82.6 (1)			
Cr-S-C	94.4 (2)	95.6 (6)			
Cr-O-N	121.9 (4)	117.7 (7)			

[a] The present structure. [b] Reference 1. [c] References 39 and 41. [d] References 40 and 42. [e] Reference 30.

the electronegative N and O atoms of the thiohydroximate chelate rings are given in Table VII. With the exception of the hydrogen bond between the oxygen of water 16 and its symmetry-related atom, all the hydrogen bonds are in the range 2.6–3.1 Å and are considered to be medium to weak bonds.[45] The O atom of water 16, which represents both the $H_3O_2^-$ anion oxygens, forms a very short hydrogen bond (2.29 (2) Å) with its symmetry-related oxygen atom to give a discrete $H_3O_2^-$ ion.

The $H_3O_2^-$ ion forms weak hydrogen bonds to water molecules 1 and 7, which bridge sodium ions 1 and 2 such that the $H_3O_2^-$ ion is surrounded by four sodium ions at a distance of 4.1–4.9 Å (Figure 4). Two of the (symmetry related) hydrogen atoms of the $H_3O_2^-$ ion were easily found in the difference Fourier. The central hydrogen atom was not seen but symmetry considerations imply that it lies on, or is disordered about, the inversion center. The short O–O distance would seem to suggest a symmetric hydrogen bond, with the central hydrogen on the inversion center. Even when corrected for thermal motion (using the independent model[37]—a large overcorrection), the O–O distance is 2.377 (12) Å, a distance that is still among the shortest known hydrogen bonds.[45,47] Other short hydrogen bonds in the range 2.35–2.45 Å have been reported for several acid salts of carboxylic acids and have been reviewed by Speakman.[48] The central hydrogen ion has a coordination number of 2; the next nearest oxygen atom (water 1) is 3.055 (8) Å away. These results parallel other reports of short hydrogen bonds in which the hydrogen ions have a coordination number of 2[46] and in most cases lie on a special position.[48]

It is interesting to compare the structure of the $H_3O_2^-$ anion with that of the isoelectronic bifluoride ion (HF_2^-), especially since F^- and OH^- have very close crystal and effective ionic radii[49] (1.15 and 1.28 Å for the fluoride ion and 1.18 and 1.32 Å for the hydroxide ion, respectively). In the alkali salts the bifluoride ion (HF_2^-) crystallizes in the symmetric linear form, with an F–F separation of 2.264 (3) Å,[50] 2.277 (6) Å,[51] and 2.269 (5) Å for the Na^+,[50] K^+,[51] and NH_4^+[52] salts, respectively. The HF_2^- ion exists in a linear, asymmetric form in the *p*-toluidinium salt with an F–F distance of 2.260 (4) Å, as has been determined by X-ray and neutron diffraction.[53] These F–F distances of 2.26–2.28 Å compare well with that of the O–O distance of 2.29 (2) Å in the $H_3O_2^-$ anion, where a distance of about 2.32 Å would be expected from ionic radii comparisons.

Summary

The structure of the tris(thiohydroximato)chromate(III) anion shows relatively little change in complex or ligand geometry from the thiohydroxamate complexes. The small changes observed correspond to a *lengthening* of the Cr–O, Cr–S, C–S, and N–O bonds and a *contraction* of the C–N bond as the neutral complex is deprotonated. This shows that the singly deprotonated thiohydroxamate group has substantially the same bonding (a formal negative charge on S and O and a C–N double bond) as that in the doubly deprotonated thiohydroximate group. In addition to reporting the first thiohydroximato complex, we have also found the first example of a discrete $H_3O_2^-$ anion, the structure of which compares closely with that of the isoelectronic HF_2^- anion.

Acknowledgment. The structural aspects of this research are supported by the National Science Foundation. Support for the microbial iron transport research is provided by the NIH (Grant AI 11744).

Registry No. $Na_2[(C_2H_5)_3(CH_3)N][Cr(C_6H_5C(S){=}N(O))_3]\cdot{}^1/_2NaH_3O_2\cdot 18H_2O$, 70644-12-1; tris(thiobenzohydroxamato)chromium(III), 61477-67-6.

Supplementary Material Available: Structure factor amplitudes and Tables III (amplitudes of vibrations), V (least-squares planes), and VIb (bond angles) (31 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 17: Freyberg, D. P.; Abu-Dari, K.; Raymond, K. N., submitted for publication.
(2) U.S.–A.I.D. Fellow.
(3) Raymond, K. N. *Adv. Chem. Ser.* **1977**, *No. 162*, 33–54.
(4) Neilands, J. B., Ed. "Microbial Iron Metabolism"; Academic Press: New York, 1974.
(5) Leong, J.; Raymond, K. N. *J. Am. Chem. Soc.* **1974**, *96*, 6628–30.
(6) Leong, J.; Raymond, K. N. *J. Am. Chem. Soc.* **1975**, *97*, 293–6.
(7) Isied, S. S.; Kuo, G.; Raymond, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 1763–7.
(8) Ito, Y.; Umino, K.; Sekiguchi, T.; Miyagishima, T.; Egawa, Y. *J. Antibiot.* **1970**, *23*, 267–70.
(9) Egawa, Y.; Umino, K.; Ito, Y.; Okuda, T. *J. Antibiot.* **1971**, *24*, 124–30.
(10) Ito, Y.; Umino, K.; Sekiguchi, T.; Miyagishima, T.; Egawa, Y. *J. Antibiot.* **1971**, *24*, 131–4.
(11) Miyagishima, T.; Yamaguchi, T.; Umino, K. *Chem. Pharm. Bull.* **1974**, *22*, 2283–93.
(12) Itoh, S.; Inuzuka, K.; Suzuki, T. *J. Antibiot.* **1970**, *23*, 542–5.
(13) Shirahata, K.; Deguchi, T.; Hayashi, T.; Matsubara, I.; Suzuki, T. *J. Antibiot.* **1970**, *23*, 546–50.
(14) Shirahata, K.; Hayashi, T.; Matsubara, I. *J. Antibiot.* **1971**, *24*, 140–1.
(15) Del Rio, L. A.; Lopez, G. J.; Olivares, L.; Mayer, F. *Antimicrob. Agents Chemother.* **1972**, *2*, 189–94.
(16) Martinez-Molim, E.; de Rio, L. A.; Olivares, J. *J. Appl. Bacteriol.* **1976**, *41*, 69–74.
(17) Miyamura, S.; Ogasawara, N.; Otsuka, H.; Niwayama, S.; Tanaka, H.; Take, T.; Uchiyama, T.; Nakazawa, H.; Abe, K.; Koizumi, K. *J. Antibiot.* **1972**, *25*, 369–70.
(18) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *25*, 925–46.
(19) Nagata, K.; Mizukami, S. *Chem. Pharm. Bull.* **1966**, *14*, 1263–72.
(20) Nagata, K.; Mizukami, S. *Chem. Pharm. Bull.* **1967**, *15*, 70–6.
(21) Jensen, K. A.; Buchardt, O.; Christophersen, C. *Acta Chem. Scand.* **1967**, *21*, 1936–41.
(22) Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* **1977**, *16*, 807–12.
(23) Murray, K. S.; Newman, P. J.; Gatehouse, B. M. *Aust J. Chem.* **1978**, *31*, 983–92.
(24) Leong, J.; Bell, S. J. *Inorg. Chem.* **1978**, *17*, 1886–92.
(25) Mizukami, S.; Nagata, K. *Chem. Pharm. Bull.* **1966**, *14*, 1249–55.
(26) Collman, J. P., Kittleman, E. T. *Inorg. Synth.* **1966**, *8*, 149–53.
(27) The Enraf-Nonius Fortran IV system operates the CAD-4 diffractometer. In addition to locally written programs for the CDC 7600, the following programs or modifications were used: Zalkin's FORDAP Fourier program; Ibers' NUCLS, a group least-squares version of the Busing–Levy ORFLS program; ORFFE, a function and error program by Busing and Levy; ORTEP by Johnson, RBANG, a program to handle rigid groups; MULTAN, a program series for direct method phase determination by Germain, Main, and Woolfson.
(28) The intensities of a unique set of reflections ($+h,\pm k,\pm l$) with $2° < 2\theta < 50°$ were measured by using the θ–2θ scan technique [the duplicates were also measured for ($0,\pm k,\pm l$) as a check]. The θ scan angle was calculated as ($0.75 + 0.35 \tan\theta$). An aperture with a height of 4 mm and a variable width [width (mm) = $2.50 + 0.50 \tan\theta$] was located 173 mm from the crystal. For each reflection the scan angle was extended 25% on either side to estimate the background count. The scan time was variable, with a maximum of 80 s. The intensities of three standard reflections were monitored regularly and showed no significant fluctuations. Three orientation standard reflections were also monitored regularly and showed no change in setting angle greater than 0.1° in any axis. An attenuator decreasing the intensity of the diffracted beam by a factor of 18.17 was inserted into the beam when the prescan indicated an intensity too high for accurate counting ($I > 50\,000$ counts/s).
(29) Baker, E. C.; Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, *14*, 1376–9.
(30) Abu-Dari, K.; Ekstrand, J. D.; Freyburg, D. P.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 108–12.
(31) Definitions of the indicators are $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)^2)/\sum wF_o^2]^{1/2}$ and the error in an observation of unit weight is $[(\sum w(|F_o| - |F_c|)^2)/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v the number of variables.
(32) Cromer, D. T.; Mann, B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321–4.
(33) Stewart, R. F.; Davidson, E. T.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.
(34) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17–23.
(35) Lonsdale, K., Ed. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962.
(36) Supplementary material.
(37) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFFE, a FORTRAN Crystallographic Function and Error Program", Report ORNL-TM-306; AEC: Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
(38) Gottlicher, S.; Ochsenreiter, P. *Chem. Ber.* **1974**, *107*, 398–413.
(39) Sato, T.; Nagata, K.; Shiro, M.; Koyama, H. *Chem. Commun.* **1966**, 192.
(40) Sato, T.; Nagata, K.; Tsukuda, Y.; Shiro, M.; Koyama, H. *Chem. Commun.* **1967**, 215–6.
(41) Sato, T.; Shiro, M.; Koyama, H. *J. Chem. Soc. B* **1968**, 989–94.

(42) Sato, T.; Tsukuda, Y.; Shiro, M.; Koyama, H. *J. Chem. Soc. B* **1969**, 125–30.
(43) Oosthock, V. A. N. "Molecular Structure and Dimensions"; Kennard, O., Watson, D. G., Allen, F. H., Isaacs, N. W., Motherwell, W. D., Pattersen, R. C., Town, W. G., Eds.; Vitegerets Mij: Utrecht, 1972; Vol. 1.
(44) Larsen, I. K. *Acta Chem. Scand.* **1971**, *25*, 2408–9.
(45) Brown, I. D. *Acta Crystallog.* **1976**, *732*, 24–31.
(46) Caff, M.; Ferraris, G. *Acta Crystallog., Sect. B* **1976**, *32*, 2754–6.
(47) Novak, A., *Struct. Bonding (Berlin)* **1974**, *18*, 177–216.
(48) Speakman, J. C. *Struct. Bonding (Berlin)* **1972**, *12*, 141–99.
(49) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751–67.
(50) McGaw, B. L.; Ibers, J. A. *J. Chem. Phys.* **1963**, *39*, 2677–84.
(51) Ibers, J. A. *J. Chem. Phys.* **1964**, *40*, 402–4.
(52) McDonald, T. R. R. *Acta Crystallogr.* **1960**, *13*, 113–24.
(53) Williams, J. M., Schneemeyer, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 5780–1.

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
Guelph Campus, Univeristy of Guelph, Guelph, Ontario, Canada N1G 2W1

Structural Studies of Steric Effects in Phosphine Complexes. 5.[1] Synthesis and Crystal and Molecular Structures of the Dimers Bis(acetato)(tricyclohexylphosphine)mercury(II) and Bis(acetato)(tri-*o*-tolylphosphine)mercury(II)

ELMER C. ALYEA,* SHELTON A. DIAS, GEORGE FERGUSON,* MASOOD A. KHAN, and PAUL J. ROBERTS

Received March 5, 1979

X-ray crystallographic studies have been carried out on two new mercury compounds containing bulky phosphine ligands $[HgPCy_3(OAc)_2]_2$ (I) and $[HgP(o\text{-tol})_3(OAc)_2]_2$ (II). Crystals of I and II are monoclinic, with two dimeric molecules in each unit cell. Cell data for I are $a = 9.714$ (1) Å, $b = 15.163$ (3) Å, $c = 16.686$ (2) Å, $\beta = 93.91$ (1)°, and space group $P2_1/c$; for II the cell data are $a = 10.485$ (8) Å, $b = 21.64$ (2) Å, $c = 10.762$ (8) Å, $\beta = 97.47$ (5)°, and space group $P2_1/n$. For both compounds, three-dimensional intensity data were collected by four-circle diffractometer measurements and refinement was by full-matrix least-squares calculations. At convergence $R_F = 0.040$ and $R_{wF} = 0.044$ for 3181 observed reflections for I; for II the corresponding values are $R_F = 0.085$ and $R_{wF} = 0.074$ for 1398 observed reflections. The dimeric molecules are isostructural with $[HgPCy_3(NO_3)_2]_2$; a hitherto unknown acetato bridging mode with only one oxygen atom from each of two acetato groups linking pairs of mercury atoms is found. In both molecules, the predominant feature of the mercury coordination is the presence of three nearly coplanar strong bonds: Hg–P = 2.378 (1), Hg–O = 2.194 (5) and 2.292 (4) Å in I; Hg–P = 2.41 (1), Hg–O = 2.36 (4) and 2.20 (4) Å in II. A fourth weaker bond (Hg–O = 2.523 (4) Å in I and 2.73 (4) Å in II) forms the bridge to the other centrosymmetrically related mercury atom; sixfold coordination about mercury is achieved in each case by weaker intramolecular interactions with acetato oxygens (Hg–O = 2.63–2.92 Å). Both compounds exist as monomers in dichloroethane solution. Cone angle calculations are made for PCy_3 ($\theta = 179°$) and $P(o\text{-tol})_3$ ($\theta = 191°$) and ligand profiles are given for the bulky phosphines in I and II.

Introduction

In an attempt to relate steric and electronic properties of the ligand to molecular stereochemistry, a systematic investigation of the bulky tertiary phosphine derivatives of mercury(II) is in progress in our laboratories. We have already reported the crystal structures of $[HgPCy_3(SCN)_2]_n$,[2] $[HgPCy_3(NO_3)_2]_2$,[3] and $HgP(t\text{-}Bu)_3(OAc)_2$[4] and have developed the concept of a ligand profile[5] which provides cone angle[6] data and rationalizes the effects of steric properties of bulky phosphine ligands such as PCy_3, $P(t\text{-}Bu)_3$, $P(o\text{-tolyl})_3$, and $P(\text{mesityl})_3$.[7] To provide data for cone angle and ligand profile calculations of PCy_3 and $P(o\text{-tolyl})_3$ ligands, we prepared complexes of these ligands with $Hg(OAc)_2$. Molecular weight determinations (see Experimental Section) indicated that these structures are monomeric in solution. However, our X-ray analyses show unequivocally that the solid-state structures are dimeric, $[HgPCy_3(OAc)_2]_2$ (I) and $[Hg(P(o\text{-tolyl})_3)(OAc)_2]_2$ (II), with a unique mode of acetate bridging, and are essentially isostructural with $[HgPCy_3(NO_3)_2]_2$.[3]

Experimental Section

$[HgPCy_3(OAc)_2]_2$ (I) was prepared by adding a solution of PCy_3 in dichloromethane to a suspension of $Hg(OAc)_2$ in dichloromethane in a 1:1 molar ratio. After stirring for 2 h, the resulting clear, colorless solution was concentrated on a rotary evaporator. The product so obtained was washed with ether and recrystallized from dichloromethane/hexane as white crystals; yield 98%, mp 149–150 °C dec. Anal. Calcd for $C_{22}H_{39}O_4PHg$: C, 44.11; H, 6.51. Found: C, 43.93; H, 6.56. X-ray analysis was done on a sample recrystallized from ethanol/hexane. I has molar conductance in dry nitromethane (10^{-3} M solution) of 22 Ω^{-1} cm^2. The molecular weight by osmometry in dichloroethane (ca. 10^{-3} M solution) is 627 (calcd 599). The ^{1}H NMR spectrum of I in deuteriochloroform showed a broad unresolved multiplet between δ 0.92 and 2.83 ppm, downfield from 0.63 and 2.33 ppm in free PCy_3, and a sharp singlet (due to acetato methyl protons) at δ 2.01 ppm. The ^{31}P NMR spectrum of I in dichloromethane solution at ambient temperature shows a signal at 60.5 ppm (δ, downfield from external 85% H_3PO_4 as reference) with satellite peaks due to mercury-199; $^1J(^{199}Hg-^{31}P) = 7461$ Hz. Acetato infrared spectral bands (in cm^{-1}) occur at 1605 (vs), 1592 (vs), 1578 (vs), and 1370 (s, br) in the solid state (halocarbon mull/CsI plates) and at 1608 (m, sh), 1575 (vs, br), 1402 (s, br), and 1340 (w) in dichloromethane solution. The synthesis and characterization of II and a number of other $Hg(PR_3)_n(OAc)_2$ (n = 1, 2) complexes have been reported elsewhere.[8] II is also a nonconductor in nitromethane and a monomer in dichloroethane.

Crystallographic Measurements. Initial film examination of $[HgPCy_3(OAc)_2]_2$ (I) and $[HgP(o\text{-tol})_3(OAc)_2]_2$ (II) crystals provided approximate cell dimensions. The space group for I was determined to be $P2_1/c$ (C_{2h}^5, No. 14) from the systematic absences ($h0l$ if $l = 2n + 1$, $0k0$ if $k = 2n + 1$); for II space group $P2_1/n$ (an alternate setting of $P2_1/c$ with equivalent positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$) was determined by the systematic absences ($h0l$ if $h + l = 2n + 1$, $0k0$ if $k = 2n + 1$). In each case accurate cell parameters (Table I) and the crystal orientation matrix were determined by a least-squares treatment of the diffractometer setting angles of 12 reflections which were widely separated in the reciprocal space. Three-dimensional intensity data were collected in our usual way[3] by using a computer-controlled Hilger and Watts Y290 four-circle diffractometer with monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation; details are given in Table I. The crystals of both compounds turned black during data collection and the intensities of three standard reflections monitored every 100 reflections decreased by 35% for I and 15% for II. This was allowed for by appropriate scaling.[9] Intensity data for I and II were corrected for Lorentz, polarization,[10] and absorption factors;[11] only data with $I > 3\sigma(I)$ were used in structure solution and refinement.

0020-1669/79/1318-2433$01.00/0 © 1979 American Chemical Society