comparison of the spectra shown for *m*-nitrobenzoic acid and for the nitrated trinuclear compound that some of the signals in the latter case show slightly more complex splittings than those in the former. There are at least two possible reasons for this. It could be due to higher order splittings that are manifested more clearly because of the somewhat different chemical shifts in the cluster cation or to slightly better resolution in the spectrum of the cluster cation. It must also be noted that geometric isomers that may not interconvert rapidly on the NMR time scale may exist in the nitrated cluster. This isomerism would arise because for each $C_6H_4NO_2$ group two orientations (right or left) are possible. Most likely the only important effect (if any) of this on the NMR spectrum would arise from the influence of one $C_6H_4(NO_2)CO_2$ group on the other one spanning the same Mo–Mo bond. For such a pair the NO_2 groups could be syn or anti.

Acknowledgment. We thank the National Science Foundation and the U.S.-Israel Binational Science Foundation for support.

Registry No. **1**, 92575-20-7; **3**, 92545-28-3; $[Mo_3O_2(O_2C\text{-}m\text{-}NO_2C_6H_4)_6(H_2O)_3]^{2+}$, 92622-28-1; $Mo_2(O_2CC_6H_5)_4$, 24378-22-1; $Mo_2(OAc)_4$, 14221-06-8; $W(CO)_6$, 14040-11-0; $[C_6H_5C(O)O]_2$, 94-36-0; benzoic acid, 65-85-0.

Supplementary Material Available: Tables of anisotropic thermal parameters, complete bond distances and angles, and the observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

Comparative Study of Structures, Including Jahn–Teller Effects, in the Saccharinate Complexes, $[M(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$, of Chromium and Zinc, as well as Other Divalent Metal Ions

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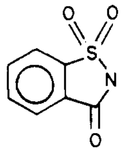
Received January 26, 1984

The chromium(II) and zinc(II) complexes of saccharine, $[M(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$, have been prepared and their structures determined by X-ray crystallography. The chromium compound shows clear evidence of Jahn–Teller distortion. When the results for the two new compounds are combined with results in the literature for analogous compounds of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II}, a broad picture of structural properties vs. d-orbital population for high-spin divalent ions for the first transition series is provided. For the series Mn, Fe, Co, Ni, and Zn the expected trends are seen in the bond lengths as the high-spin configurations change, with maxima at Mn and Zn and a minimum at Ni. The bond lengths for the Cu compound deviate enormously (one Cu–O distance being greater, the other Cu–O and the Cu–N distances being less) from the values interpolated between the Ni and Zn data. For the Cr compound, the Jahn–Teller distortions take the same form as those for Cu, but they are only about half as large. The chromium and zinc compounds are isomorphous, crystallizing in space group $P2_1/c$ with $Z = 2$. The cell constants for $ZnC_{14}H_{20}O_{12}N_2S_2$ are $a = 7.934$ (1) Å, $b = 16.118$ (3) Å, $c = 7.691$ (1) Å, and $\beta = 99.90$ (1)° and for $CrC_{14}H_{20}O_{12}N_2S_2$ are $a = 8.042$ (4) Å, $b = 16.032$ (8) Å, $c = 7.804$ (4) Å, and $\beta = 100.90$ (4)°.

Introduction

Several years ago we became interested in the possibility of preparing compounds of Cr_2^{4+} and Mo_2^{4+} using the anion of saccharine (**1**) as a bridging ligand. In the course of that work, which will be reported later, we obtained a mononuclear compound, $Cr(C_7H_4NO_3S)_2(H_2O)_6$, whose structure we determined by X-ray crystallography. We then noted that a little earlier the structure of the analogous copper(II) compound had been the subject of a preliminary report.[1] Complexes of both of the high-spin ions, Cr^{2+} (d^4) and Cu^{2+} (d^9), are well-known to be subject to Jahn–Teller effects of similar character, i.e., due to an odd number of e_g electrons, which in an (idealized) octahedral environment give rise to an E ground state.[2] Both of the saccharinate structures suggested that even though the coordination sphere in these compounds, which consists of two saccharinate nitrogen atoms and four water molecules, could not provide a truly octahedral ligand field, geometric distortions of the types that are loosely, if not rigorously, called Jahn–Teller distortions were evident. However, detailed discussion of these structures was not possible since no structure of an analogous compound with a cation not subject to a Jahn–Teller effect was available for comparison.



1

To supply a suitable comparison structure, we undertook the preparation and crystallographic study of the zinc saccharinate. In the meantime, however, other workers reported the structures first of the manganese[3] compound and then of the iron, cobalt, and nickel compounds[4] as well as full details of the copper structure.[4] With all of the structural data now available, it is possible to make an extensive correlation of the structural changes in a homologous series of complexes as a function of their d^n configurations. In particular, the Jahn–Teller distortions for the Cr^{II} and Cu^{II} compounds can be placed in the context of a broad range of homologous structures for ions that do not undergo Jahn–Teller distortions.

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Table I. Crystallographic Data and Parameters

formula	$ZnC_{14}H_{20}O_{12}N_2S_2$	$CrC_{14}H_{20}O_{12}N_2S_2$
fw	537.82	524.45
space group	$P2_1/c$	$P2_1/c$
syst absences	$h0l$ ($l \neq 2n$), $0k0$ ($k \neq 2n$)	$h0l$ ($l \neq 2n$), $0k0$ ($k \neq 2n$)
a, Å	7.934 (1)	8.042 (4)
b, Å	16.118 (3)	16.032 (8)
c, Å	7.691 (1)	7.804 (4)
β, deg	99.90 (1)	100.90 (4)
V, Å^3	968.9 (3)	988.1 (8)
Z	2	2
d_{calcd}, g/cm^3	1.832	1.763
cryst size, mm	0.2 × 0.4 × 0.5	0.1 × 0.1 × 0.5
μ(Mo Kα), cm^{-1}	15.608	8.330
abs cor	semiempirical (ψ scan)	none
data collcn instrum	$P\bar{1}$	$P\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)	Mo Kα
no. of orientation reflcns; range (2θ), deg	15; 18–27	15; 18–27
temp, °C	5	5
scan method	ω–2θ	ω–2θ
data collcn range (2θ), deg	2–55 ($+h,+k,\pm l$)	4–50 ($+h,+k,\pm l$)
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1893, 1814	1547, 1317
no. of parameters refined	182	182
R^a	0.028	0.030
$R_w{}^b$	0.042	0.043
quality-of-fit indicator^c	1.013	0.907
largest shift/esd, final cycle	0.26	0.27
largest peak, e/Å^3	0.497	0.252

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{observns} - N_{parameters})]^{1/2}$.

Experimental Section

All reactions using chromium(II) species were done under a nitrogen atmosphere with standard Schlenk type techniques.

Preparations. Stock Aqueous Chromium(II) Solution. Chromium metal powder (1.1 g) was added to 50 mL of 0.6 M HCl. The mixture was stirred at 40 °C for 6 h. The undissolved chromium metal was removed by filtering through Celite, leaving a clear light blue solution.

Chromium Saccharinate. Sodium saccharinate dihydrate (0.26 g) was added with constant stirring to 10 mL of a stock aqueous chromium(II) solution. A yellow precipitate formed almost immediately. It was filtered, quickly washed with small portions of cold water, and dried.

Crystals were formed by adding 0.26 g of sodium saccarinate and then 25 mL of acetone to the filtrate. This solution was left at 10 °C.

Zinc Saccharinate. Zinc chloride (1.10 g, 8.0 mmol) was dissolved in 25 mL of water. To this solution was slowly added sodium saccharinate dihydrate (4.0 g, 18 mmol) dissolved in 10 mL of water with constant stirring. A white precipitate formed. The reaction mixture was cooled to 0 °C for 1 h and then filtered. The solid was washed with small portions of cold water and was dried. It gave 3.7 g of zinc saccharinate (88%). Crystals were grown as in the chromium case.

X-ray Crystallography. The structure determinations were carried out by using experimental methods essentially similar to those reported earlier.[5,6] The pertinent crystal characteristics and other numerical information are given in Table I. For the zinc compound the crystal was mounted on the end of a glass fiber, but the crystal of the chromium compound was sealed in a thin-walled glass capillary. The chromium structure was solved first by using direct methods in the form of the MULTAN program. The zinc compound was treated by using the coordinates of the chromium compound to begin. In each case the hydrogen atoms were located in a difference electron density map after the heavy-atom structure had been refined. Refinement was then resumed with inclusion of the hydrogen atoms, which were assigned isotropic thermal parameters. The figures of merit are given in Table I, and positional parameters along with isotropic thermal parameters for both compounds are listed in Table II.

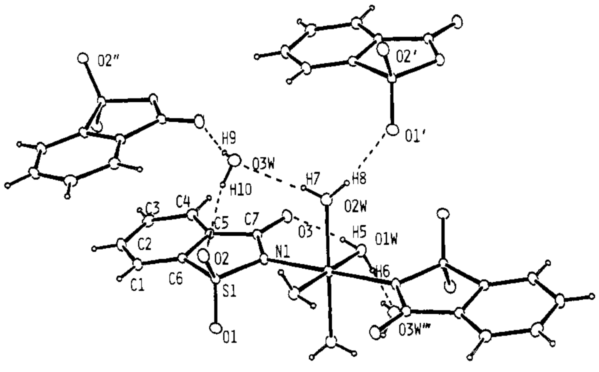

Figure 1. Molecule of $M(C_7H_4NO_3S)_2(H_2O)_4$ (M = Cr, Zn) showing each type of hydrogen bond. The symmetry operators relating the various units, U, or portions thereof, are as follows: (U) x, y, z; (U') $-1 + x, y, z$; (U'') $x, -\frac{1}{2} - y, \frac{1}{2} + z$; ($U'''$) $x, y, -1 + z$.

Results and Discussion

Table III gives the important bond distances and angles for both the zinc and chromium compounds. The structure of the chromium compound is depicted in Figure 1, and the labeling scheme, which is applicable to both compounds, is there defined. The general features of these structures have already been discussed in earlier reports[3,4] from other laboratories and need not be discussed again in detail here. The coordination of the metal ion is "octahedral" in the loose sense of that term, with a centrosymmetric arrangement of two saccharinate nitrogen atoms and four water molecules. The ligand–metal–ligand angles are all close to the ideal values of 90 or 180°. In addition to these molecules, which contain the water molecules W(1) and W(2), there is a third type of water molecule, W(3), that lies between the metal complexes and contributes to the stability and precision of the crystal structure by forming four hydrogen bonds, donating two hydrogen atoms, and accepting two. A complete list of the hydrogen bonds formed by all of the water molecules is given in Table IV.

There is one very interesting aspect of this general structure that has not previously been discussed, namely, that the two coordinated water molecules, W(1) and W(2), have markedly different orientations relative to the metal ion. It is well recognized that there is a whole range of potential orientations for a coordinated water molecule, with the limits of the range being defined by the so-called *flat* and *pyramidal* cases. In the idealized flat case the M–O bond lies in the plane of the water molecule; all four atoms are coplanar. In the pyramidal case the M–O and two H–O bonds are directed roughly at the vertices of a tetrahedron. As several recent surveys show, much remains to be learned, both factually and theoretically, about the frequency of occurrence of structures at and between these extremes and about the determinative factors.[7,8]

In the present series of compounds we find within one molecule, side by side, the two limiting cases. W(2) is essentially flat while W(1) is highly pyramidal.[9] It would

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(9) The deviations of O(2W) from the plane defined by M, H(7), and H(8) are 0.003 (3) and 0.007 (2) Å for the Cr and Zn compounds, respectively. The deviations of O(1W) from the M, H(5), H(6) plane are 0.274 (3) and 0.302 (2) Å for the Cr and Zn compounds, respectively.

Table II. Positional Parameters and Their Estimated Standard Deviations[a] for $M(C_7H_4NO_3S)_2(H_2O)_4 \cdot 2H_2O$ (M = Cr, Zn)

	M = Cr				M = Zn			
atom	*x*	*y*	*z*	*B*, Å^2	*x*	*y*	*z*	*B*, Å^2
M	0.000	0.000	0.000	1.58 (1)	0.000	0.000	0.000	1.574 (6)
S(1)	0.3410 (1)	−0.05780 (4)	0.2865 (1)	1.56 (1)	0.34785 (7)	−0.05791 (3)	0.28097 (6)	1.327 (9)
O(1W)	−0.0945 (3)	−0.0948 (1)	−0.1659 (3)	2.17 (5)	−0.0997 (2)	−0.0942 (1)	−0.1673 (2)	1.97 (3)
O(1)	0.4502 (3)	−0.0098 (1)	0.1999 (3)	2.38 (5)	0.4611 (2)	−0.0104 (1)	0.1929 (2)	2.10 (3)
O(2W)	−0.1910 (3)	−0.0382 (2)	0.1880 (3)	3.76 (6)	−0.1741 (2)	−0.0349 (1)	0.1745 (2)	2.86 (4)
O(2)	0.2861 (3)	−0.0189 (1)	0.4329 (3)	2.21 (5)	0.2900 (2)	−0.0188 (1)	0.4299 (2)	1.92 (3)
O(3W)	−0.0075 (3)	−0.1131 (1)	0.5081 (3)	2.57 (5)	−0.0061 (2)	−0.1124 (1)	0.4967 (2)	2.32 (3)
O(3)	0.0571 (3)	−0.2157 (1)	0.0477 (3)	2.24 (4)	0.0602 (2)	−0.2152 (1)	0.0446 (2)	2.00 (3)
N(1)	0.1762 (4)	−0.0909 (2)	0.1462 (3)	1.64 (5)	0.1819 (2)	−0.0905 (1)	0.1407 (2)	1.47 (3)
C(1)	0.5763 (4)	−0.1751 (2)	0.4593 (4)	1.94 (6)	0.5837 (3)	−0.1748 (1)	0.4532 (3)	1.75 (4)
C(2)	0.6152 (4)	−0.2594 (2)	0.4840 (4)	2.25 (7)	0.6221 (3)	−0.2587 (2)	0.4785 (3)	2.02 (4)
C(3)	0.5059 (5)	−0.3191 (2)	0.4003 (4)	2.38 (7)	0.5128 (3)	−0.3187 (1)	0.3952 (3)	2.05 (4)
C(4)	0.3566 (5)	−0.2989 (2)	0.2887 (4)	2.04 (6)	0.3611 (3)	−0.2983 (1)	0.2839 (3)	1.82 (4)
C(5)	0.3177 (4)	−0.2151 (2)	0.2606 (4)	1.68 (6)	0.3224 (3)	−0.2149 (1)	0.2562 (3)	1.41 (4)
C(6)	0.4279 (4)	−0.1558 (2)	0.3468 (4)	1.53 (6)	0.4338 (3)	−0.1557 (1)	0.3414 (3)	1.35 (4)
C(7)	0.1712 (4)	−0.1757 (2)	0.1419 (4)	1.69 (6)	0.1748 (3)	−0.1749 (1)	0.1376 (3)	1.40 (4)
H(1)	0.643 (4)	−0.135 (2)	0.520 (4)	1.2 (6)*	0.651 (3)	−0.140 (2)	0.508 (3)	1.7 (5)*
H(2)	0.724 (4)	−0.274 (2)	0.560 (4)	2.2 (7)*	0.718 (3)	−0.273 (2)	0.544 (3)	2.1 (5)*
H(3)	0.532 (4)	−0.368 (2)	0.413 (4)	2.3 (7)*	0.534 (4)	−0.368 (2)	0.408 (3)	2.4 (6)*
H(4)	0.291 (5)	−0.343 (2)	0.233 (4)	2.7 (8)*	0.287 (3)	−0.343 (2)	0.229 (3)	2.4 (6)*
H(5)	−0.074 (5)	−0.139 (2)	−0.111 (5)	3.8 (9)*	−0.066 (4)	−0.131 (2)	−0.118 (4)	3.9 (7)*
H(6)	−0.070 (5)	−0.098 (2)	−0.251 (4)	2.5 (8)*	−0.076 (4)	−0.093 (2)	−0.266 (4)	4.0 (7)*
H(7)	−0.164 (5)	−0.056 (3)	0.253 (5)	5 (1)*	−0.134 (5)	−0.063 (2)	0.251 (4)	5.3 (9)*
H(8)	−0.289 (7)	−0.033 (3)	0.183 (6)	6 (1)*	−0.273 (4)	−0.032 (2)	0.162 (4)	3.9 (7)*
H(9)	0.023 (5)	−0.158 (3)	0.504 (4)	4 (1)*	0.020 (4)	−0.343 (2)	0.002 (3)	3.7 (7)*
H(10)	0.062 (4)	−0.090 (2)	0.503 (4)	1.4 (6)*	0.082 (4)	−0.091 (2)	0.490 (4)	4.4 (8)*

[a] Estimated standard deviations in the least significant digits are shown in parentheses. Starred values are actual *B*'s.

Table III. Important Bond Distances (Å) and Bond Angles (deg) and Their Estimated Standard Deviations[a] for $M(C_7H_4NO_3S)_2(H_2O)_4 \cdot 2H_2O$ (M = Cr, Zn)

	M = Cr	M = Zn
	Distances	
M-N(1)	2.196 (3)	2.201 (2)
-O(1W)	2.048 (3)	2.058 (2)
-O(2W)	2.396 (4)	2.159 (2)
	Angles	
N(1)-M-O(1W)	87.8 (1)	88.13 (6)
-O(2W)	86.4 (1)	87.53 (7)
O(1W)-M-O(2W)	89.6 (1)	88.75 (7)

[a] Estimated standard deviations of individual distances and angles are given in parentheses for the least significant digits.

appear that the two different behaviors can be attributed to the role of hydrogen bonding. For W(2) two hydrogen bonds are formed, one intramolecularly to a sulfonyl oxygen atom, O(1), and another to a neighboring water molecule, W(3). For W(1), there is a rather strong intramolecular bond to the carbonyl oxygen atom, O(3), as well as another one to W(3). In the one case these H bonds are compatible with the flat orientation of the water molecule and in the other with a markedly pyramidal one. Whether it is justified to believe that H-bond optimization actually *causes* these orientations is, of course, a moot point, but such a belief is consistent with the structural data.

As a general observation on this class of compounds, and the structure they adopt, we note that opportunities are presented here for further studies aimed at elucidating some basic questions concerning the electronic structures of transition-metal compounds. Some specific observations along this line are the following:

1. The compounds are rather easy to obtain in crystalline form; the crystals diffract X-rays extremely well; it is likely that crystals well suited to neutron diffraction could be obtained.
2. These favorable crystallographic characteristics would probably facilitate the collection of diffraction data for electron density studies, including the mapping of spin density by use of polarized neutron diffraction.
3. In preliminary trials we have found that these compounds tend to cocrystallize as solid solutions. In this way materials particularly useful for the study of properties of the magnetically active ions as a function of dilution are thus available.

Trends in Ionic Size and Shape. With the entire series of compounds now structurally characterized, it is possible to see very clearly the way in which the radii and stereochemical preferences of the divalent ions of the first transition series change with d-orbital configuration. Of course, a general picture of these trends has long been available,[10] but the present

Table IV. Hydrogen Bonds[a] for $M(C_7H_4NO_3S)_2(H_2O)_4 \cdot 2H_2O$ (M = Cr, Zn) (Hydrogen Atom Located Nearer the Atom Referred to as "Donor")

				donor to acceptor dist, Å		acceptor to H dist, Å		angle at H, deg	
donor	H	acceptor	acceptor coord	Cr	Zn	Cr	Zn	Cr	Zn
O(1W)	H(5)	O(3)	*x*, *y*, *z*	2.694 (3)	2.712 (2)	1.91 (4)	2.00 (3)	156 (4)	168 (3)
O(1W)	H(6)	O(3W)	*x*, *y*, −1 + *z*	2.779 (3)	2.824 (2)	2.05 (4)	2.02 (3)	177 (4)	169 (3)
O(2W)	H(7)	O(3W)	*x*, *y*, *z*	2.910 (3)	2.888 (2)	2.33 (4)	2.14 (3)	169 (5)	166 (4)
O(2W)	H(8)	O(1)	−1 + *x*, *y*, *z*	2.940 (4)	2.949 (3)	2.16 (6)	2.19 (4)	173 (4)	165 (3)
O(3W)	H(9)	O(3)	$x, -^1/_2 - y, ^1/_2 + z$	2.799 (3)	2.840 (2)	2.07 (4)	2.10 (3)	162 (4)	170 (3)
O(3W)	H(10)	O(2)	*x*, *y*, *z*	2.954 (3)	2.911 (2)	2.29 (3)	2.13 (4)	170 (3)	169 (3)

[a] Estimated standard deviations are given in parentheses for the least significant digits.

Table V. Comparison of Crystallographic and Structural Data for Seven Saccharinate Complexes

	Cr	Mn	Fe	Co	Ni	Cu	Zn
a, Å	8.042 (4)	7.955 (2)	7.929 (1)	7.908 (2)	7.918 (2)	8.384 (2)	7.934 (1)
b, Å	16.032 (8)	16.131 (6)	16.140 (2)	16.136 (2)	16.139 (3)	16.327 (2)	16.118 (3)
c, Å	7.804 (4)	7.784 (1)	7.738 (2)	7.688 (1)	7.651 (2)	7.327 (2)	7.691 (1)
β, deg	100.90 (4)	99.70 (3)	99.77 (2)	99.60 (2)	99.94 (2)	101.08 (2)	99.90 (1)
V, Å^3	988.1 (8)	984.6	975.8	967.2	963.0	984.8	968.9 (3)
M-N, Å	2.196 (3)	2.281 (1)	2.235 (2)	2.200 (1)	2.154 (1)	2.061 (2)	2.201 (2)
M-O, Å	2.396 (4)	2.219 (2)	2.159 (2)	2.124 (2)	2.096 (2)	2.489 (3)	2.159 (2)
M-O′, Å	2.048 (3)	2.162 (1)	2.099 (2)	2.060 (1)	2.042 (1)	1.956 (2)	2.058 (2)
ref	this work	3	4	4	4	4	this work

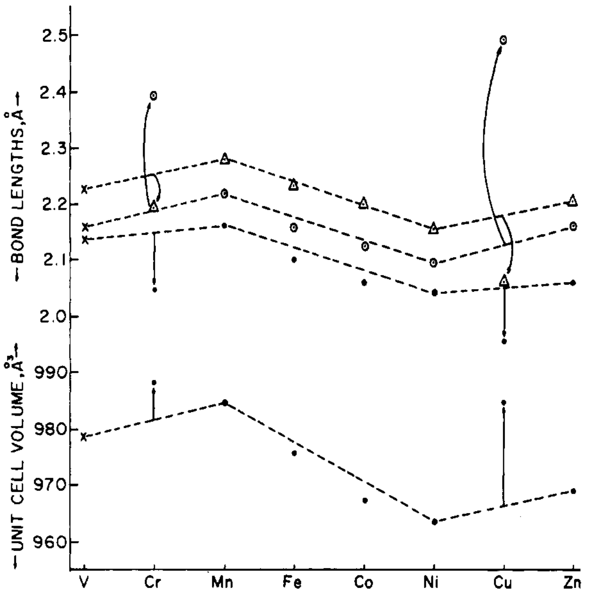

Figure 2. Variations in the structure as the metal atom changes: upper part, individual metal-ligand bond lengths (△, M-N; ○, ●, M-O); lower part, unit cell volumes. See Table V for numerical values.

series of compounds is unique (or at least highly unusual) in its completeness, precision, and constancy of crystallographic environment for all compounds. Comparative data are summarized in Table V and plotted in Figure 2.

The general qualitative pattern of bond lengths and unit cell volumes for the ions not subject to significant Jahn-Teller effects[11] is precisely that expected from the qualitative crystal field theory.[10] The points designated by X's for V^{2+} in Figure 2 are not experimental ones, since we have not succeeded in obtaining the necessary crystalline vanadium(II) saccharinate. Their positions were obtained by the reasonable (but not necessarily quantitatively correct) procedure of extrapolating lines from the data points for the manganese compound using the same slopes as those for the lines connecting the points for zinc and nickel. We did this so as to have at least a tentative estimate of the interpolated values for a hypothetical "non-Jahn-Teller" chromium compound, which then allows us to compare the behavior of the chromium(II) ion with that of the copper(II) ion.

It is clear that qualitatively the d^4 chromium(II) ion and the d^9 copper(II) ion have similar deviations from the regular pattern found in the other structures: one M-O bond and the M-N bond become shorter while the other M-O becomes very much longer. However, quantitatively, the changes are about twice as large for the copper compound as for the chromium compound. From the limited data available for a few classes of compounds in which metal ions occupy octahedral interstices in close-packed arrays of anions, e.g., MF_2, MCl_2, and KMF_3 compounds,[12] it appears that the two ions tended to have more nearly equal degrees of distortion, but the point is not clearly elucidated by the data. In any event, in these highly ionic, close-packed systems, the freedom of the Jahn-Teller ion to distort its environment is likely to be rather strongly resisted by the rather strong forces in such rigid, tightly packed structures.[13]

In terms of studying the Jahn-Teller effect, the hydrated saccharinate compounds have one obvious advantage and one obvious disadvantage. The disadvantage is perhaps more formal than real and arises from the fact that with the mixed ligand set (2 N and 4 O) no rigorously octahedral coordination sphere, and hence no rigorous electronic degeneracy, is possible. It would appear, however, that the structures which would be interpolated for the chromium and copper compounds come close enough to the ideal case that the vibronic problem envisioned in the work of Jahn and Teller[14] plays itself out according to their analysis.

The advantage of this series of compounds, aside from the obvious one that it is an isostructural series, is that the structure as a whole is a relatively forgiving or relaxing one, in the sense of tolerating considerable changes of atomic positions around the metal ions without collapsing. The overall structure is relatively open and hence flexible in its response to the electronically induced stereochemical demands of the metal ions. Interestingly, in another sense this structure is a very crisp and well-ordered one that gives crystals that diffract X-rays unusually well, thus giving excellent data for the refinement of the structure.

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Registry No. $Cr(C_7H_4NO_3S)_2(H_2O)_4 \cdot 2H_2O$, 92763-66-1; $Zn(C_7H_4NO_3S)_2(H_2O)_4 \cdot 2H_2O$, 82443-51-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, all bond distances and angles, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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(10) Dunitz, J. D.; Orgel, L. E. *Adv. Inorg. Chem. Radiochem.* **1960**, *2*, 1. This is the most comprehensive and authoritative article presenting the "post crystal field" interpretations of transition metal ion stereochemistry. In this article, radii for the M^{2+} ions are derived from several types of compounds, rather than one homologous set, and the correlations are, empirically speaking, somewhat unsatisfactory. However, the concepts presented in this article are perfectly sound and are precisely those assumed in the present discussion.

(11) Certain $t_{2g}{}^n$ configurations can, in principle, give rise to Jahn-Teller effects in octahedral complexes, but these are expected to be an order of magnitude smaller than those caused by $e_g{}^1$ and $e_g{}^3$ configurations. They have never been empirically documented, and we shall neglect them altogether.

(12) A source of data on this point is: Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Clarendon Press: Oxford, 1975.

(13) Precisely this kind of problem has been encountered in connection with the degree of irregularity exhibited by various M_6 octahedra in Chevrel phases. It has been pointed out that the shape actually observed will be the result of the joint (probably opposing) action of an *electronic effect* inherent in the M_6 octahedron and a *matrix effect*, which is the totality of the lattice forces against which movements of metal atoms must work. Cf.: Corbett, J. D. *J. Solid State Chem.* **1981**, *39*, 56.

(14) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937**, *A161*, 220.