Table II. Compounds with Metal–Boron Tridentate Hydrogen Bridges

compd	M^{z+} CN	M^{z+} IR[a]	M–B, Å	BH_4^- IR[b]	ref	comments[c]
$Sc(BH_4)_3(OC_4H_8)_2$	10	0.95	2.33 (1)	1.38	10	RT, X-ray, crys
$[C_5H_5TiCl(BH_4)]_2$	8	0.76	2.17 (1)	1.41	24	RT, X-ray, crys
$Y(BH_4)_3(OC_4H_8)_3$	11	1.14	2.58 (1)	1.44	16	23 °C, X-ray, crys
$Zr(BH_4)_4$	12	0.98	2.308 (10)	1.33	25	RT, ED, gas
$Zr(BH_4)_4$	12	0.98	2.34 (3)	1.36	26	−160 °C, X-ray, crys
$Hf(BH_4)_4$	12	0.95	2.28 (1)	1.33	27	ND, crys
$U(BH_4)_4$	14	1.22	2.52 (1)	1.30	21	RT, ND, crys
$Th[N(Si(CH_3)_3)_2]_3BH_4$	6	0.94	2.61 (3)	1.67	28	22 °C, X-ray, crys
$(C_5H_5)_2U(BH_4)_2$	12	1.17	2.61 (8)	1.44	29	RT, X-ray, crys
$U(BH_4)_4(OC_4H_8)_2$	14	1.22	2.56 (4)	1.34	30	23.5 °C, X-ray, crys
$U(BH_4)_4 \cdot O(C_2H_5)_2$	14	1.22	2.53 (2)	1.31	22	21 °C, X-ray, crys
$U(BH_4)_4 \cdot O(CH_3)_2$	14	1.22	2.53 (2)	1.31	22	23 °C, X-ray, crys
$[U(BH_4)_4 \cdot O(n\text{-}C_3H_7)_2]_2$[d]	13	1.20	2.51 (5)	1.31	23	22 °C, X-ray, crys
$[U(BH_4)_4 \cdot O(n\text{-}C_3H_7)_2]_2$[d]	14	1.22	2.52 (5)	1.30	23	22 °C, X-ray, crys
$Np(BH_4)_4$	12	1.10	2.46 (3)	1.36	31	−143 °C, X-ray, crys

[a] From Shannon[35] corrected for coordination number; IR = ionic radius in Å. [b] Obtained by subtraction of column 3 from column 4. [c] Key: RT, room temperature; X-ray, X-ray diffraction; ND, neutron diffraction; ED, electron diffraction; crys, single crystal; gas, gaseous sample. [d] Unsymmetrical dimer.

distances vs. effective ionic radii for the then available compounds.

Raymond and co-workers[35,36] have recently systematized the structural criteria for ionic bonding in $(C_5H_5)^-$, $(C_8H_8)^{2-}$, and $N[Si(CH_3)_3]_2^-$ metal complexes and have followed Pauling's approach[37] to calculate corrections for differences in coordination number for a particular ion. Following Raymond's criteria, we have correlated the structural data for doubly and triply hydrogen-bridged metal–boron bonds with ionic radii for the metal ions obtained from Shannon's table.[38]

Table I and Table II list the available data for the compounds structurally characterized. The ionic radii as given in Tables I and II were obtained from Shannon's table for the particular oxidation state of the metal ion with the coordination number closest to that found in the metal borohydride complex. Corrections for coordination number were made as described by Raymond.[35] Plots of ionic radius vs. metal–boron distance are shown in Figures 1 and 2.

The lines in Figures 1 and 2 represent a linear least-squares fit to the data which were all assigned equal weight. For bidentate coordination the slope was equal to 0.97 with a correlation coefficient of 0.98. Note that both types of bidentate coordination (polymeric type and that with terminal H atoms) were included in Figure 1 and Table I. For tridentate coordination (Figure 2, not including the Th point), the slope was equal to 1.02 with a correlation coefficient of 0.94.

Considering the uncertainties in the metal ion–boron bond lengths, the different methods, temperatures, and phases for which structures were determined, the large range of coordination number and of the periodic table covered, plus the variety of other ligands attached to the metal atom, the correlation between ionic radius and the metal–boron bond length is remarkably good. For most molecules the metal–boron bond distance can be calculated with reasonable accuracy by using the ionic bonding model. Clearly, it is not possible to draw conclusions about covalent bonding between the metal atom and the borohydride group solely from structural considerations based on the metal–boron distance.

The one compound which does not fit this correlation is $[((CH_3)_3Si)_2N]_3ThBH_4$.[28] The Th ion is formally six-coordinate in this molecule, and the ionic radius obtained for the triple-hydrogen-bridged BH_4^- group (unambiguously assigned from the infrared spectrum)[28] is much too large (Figure 2). The bis(trimethylsilyl)amide group is an extremely bulky ligand which is known to form low coordination number complexes with metal ions of large ionic radii such as the lanthanides.[39] Although this ligand acts in a monodentate manner, it appears to have a much larger *effective* coordination number due to its steric bulk. From Figure 2 one can extrapolate an *effective* coordination number ≥12 for the Th ion in $[((CH_3)_3Si)_2N]_3ThBH_4$.

From the present tabulation it appears that an ionic radius of ~1.6 ± 0.1 Å can be assigned to the borohydride ligand when it forms a bidentate bridge to the metal atom and ~1.36 ± 0.06 Å when it forms a tridentate bridge to the metal atom. The difference in energy between the various possible modes of bonding is small, and the coordination number of the metal ion and the steric hindrance by other ligands appear to determine which mode of attachment will prevail for the borohydride ligand.

Acknowledgment. I would like to thank D. H. Templeton, S. J. Simpson, R. A. Andersen, A. Zalkin, and K. N. Raymond for helpful discussions. This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-7405-Eng-48.

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Received May 1, 1980

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Some Incorrect Space Groups: An Update

Sir:

Recently,[1] we noted that seven crystal structures reported in Volume 16 of *Inorganic Chemistry* (1977) had been described in space groups of unnecessarily low symmetry. We have now completed a similar survey of Volumes 17 and 18 (1978 and 1979), with the following results.

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(1) R. E. Marsh and V. Schomaker, *Inorg. Chem.*, **18**, 2331 (1979).

Table I. Reduced Cell Dimensions for $Nb_2Br_6(SC_4H_8)_3$ and $Ta_2Br_6(SC_4H_8)_3$

	Nb	Ta
a, Å	11.948 (5)	11.99 (1)
b, Å	12.790 (7)	12.74 (1)
c, Å	8.981 (2)	8.98 (1)
α, deg	96.33 (3)	96.02 (5)
β, deg	110.88 (3)	111.36 (5)
γ, deg	100.85 (3)	100.90 (5)

We find no obvious space-group errors in Volume 17 (1978). We note, though, that the structures of the Nb_2Br_6 and Ta_2Br_6 adducts with tetrahydrothiophene, which are reported to have quite different unit-cell dimensions,[2] are in fact closely isostructural. If one chooses [010], [$\overline{11}0$], and [001] as base vectors for the niobium structure, the unit-cell dimensions agree closely with those reported for the tantalum compound, and the transformation $x' = -x + y$, $y' = -x + {}^1/_2$, $z' = z$, accompanied by a renumbering of all atoms except S(1), results in equally good agreement among the coordinates. (An exception is C(6), where the *z* coordinate for the niobium compound has undoubtedly been misprinted.) This sort of confusion points up the advisability of referring all triclinic structures to a conventionally reduced cell—which, in this case, would have been based on [$0\overline{11}$], [110], and [001] of the niobium compound and [$\bar{1}0\bar{1}$], [$0\bar{1}0$], and [001] of the tantalum compound.

Dimensions of this reduced cell are given in Table I.

In Volume 18 (1979) we find three structures that could be better described in space groups of higher symmetry than reported in the original work. In each case the increase in symmetry comes from adding a center of inversion without changing the Laue symmetry. In two of these cases the centrosymmetric description entails disorder in some regions of the structure. Details follow.

$[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$[3] (2). There are two formula units in a monoclinic cell of dimensions $a = 14.246$ (2) Å, $b = 6.904$ (1) Å, $c = 17.687$ (1) Å, and $\beta = 97.19$ (1)°. The structure was described in space group *Cc* and was refined to an *R* of 0.038 for 1171 reflections with intensities greater than 3σ. Surprising results included (1) equatorial Ru–O bond lengths ranging from 1.90 to 2.06 Å, with reported esd's of 0.02 Å, (2) C–O bond distances in the bridging acetate groups ranging from 1.16 (3) to 1.36 (2) Å, (3) C–C–O bond angles in the acetate groups ranging from 105 (2) to 134 (2)°, and (4) F–B–F angles in the BF_4^- ion ranging from 89 (3) to 134 (4)°.

Formulating the structure in *C*2/*c* involves incrementing the *x*'s by 0.076 and the *z*'s by –0.387, so that the diruthenium cation is centered at (${}^1/_4$, ${}^1/_4$, 0) and the BF_4^- anion lies on a twofold axis at $x = 0$, $z = {}^1/_4$. Refinement with anisotropic *B*'s for Ru and the carboxylate oxygen atoms, as in the earlier work, led to an *R* of 0.044 for the 1130 (sic) reflections in the supplementary *F* table. At this stage the isotropic *B*'s of the two independent F atoms were quite large, at about 10; when they were allowed to become anisotropic, two further least-squares cycles led to the *C*2/*c* model described in Tables II and III, with $R = 0.036$ for 86 parameters as compared with $R = 0.038$ for 151 parameters for the earlier *Cc* model. The *C*2/*c* model has no surprising irregularities, and the virtual[3] D_{4h} symmetry of the cation turns out to be very nearly exact.

The *B* values of the fluorine atoms are highly anisotropic and clearly reflect a rigid-body motion (or disorder) that is rather typical of BF_4 groups: for both independent F atoms the maximum amplitudes of implied libration, with mean-square displacements of 0.15–0.2 Å^2, are in directions perpendicular to the B–F bonds while the components parallel to the bonds are much smaller at 0.05–0.07 Å^2. Thus, the assumption of anisotropic *B*'s for the F atoms seems entirely appropriate and leads to a far more reasonable model for the BF_4^- group than was attained in the *Cc* refinement.

$Ru_2(O_2CCH_2CH_3)_4Cl$[3] (4). The body-centered tetragonal cell, with dimensions $a = 11.049$ (2) and $c = 7.423$ (1) Å, contains two formula units. The structure was described in space group $I\bar{4}$, with crystallographic symmetry $\bar{4}$ (S_4) imposed upon the diruthenium cations, and least-squares refinement led to $R = 0.053$ for 251 reflections with intensities greater than 3σ. Again there were large variations in bond lengths and angles, particularly for the bridging propionate groups.

The centric space group *I*4/*m* requires either that the diruthenium cation have exact 4/*m* symmetry, with the terminal methyl groups of the propionate ions lying in the mirror plane, or that these methyl groups be disordered between positions on either side of the mirror. Our first least-squares refinement was based on the former model, with the methyl carbon atom C(3) at $z = 0.0$. It led to an *R* of 0.052, slightly better than obtained in the earlier $I\bar{4}$ refinement, but the propionate distances and angles were unacceptable and a difference map clearly indicated that C(3) was misplaced. We than changed to the disordered model, and obtained convergence at $R = 0.040$ for 24 atomic parameters and 251 reflections, compared with $R = 0.053$ for 37 parameters in $I\bar{4}$; a difference map showed no notable features. As in the earlier work, our refinements included anisotropic *B*'s for Ru, Cl, and O and isotropic *B*'s for the carbon atoms; the hydrogen atoms were not included.

Final *I*4/*m* parameters are given in Table IV; and bond distances and angles are given in Table V. The only unusual value is the C(2)–C(3) distance, at 1.40 (4) Å. It may well be that the model of static disorder for C(3) is incomplete and that additional libration or, perhaps, some involvement of C(2) in the disorder is responsible for the apparent shortening of this bond.

It is not unprecedented for a disordered model in space group *I*4/*m* to be more satisfactory than an ordered model in $I\bar{4}$ (see ref 4).

***catena*-Bis[μ-(*N*-methylpiperidinium-4-thiolato)]-cadmium(II) Perchlorate Dihydrate.**[5] The body-centered tetragonal cell, with dimensions $a = 18.78$ (2) and $c = 6.66$ (1) Å, contains four formula units. The structure was described in space group $I\bar{4}$ and was refined to $R = 0.076$ for 1233 reflections. Particularly disconcerting features of the reported structure include a severely distorted ClO_4^- group, with O–Cl–O angles ranging from 81.6 (3.8)° to 120.9 (6.7)°, and an O–H···O hydrogen bond of length 2.19 (7) Å—"the shortest of all $O(ClO_4^-)$–$O(H_2O)$ distances". Indeed, such a distance is shorter, by about 0.2 Å, than any other O···O hydrogen bond of any type and is particularly surprising because the O–H stretching frequency of 3400 cm^{-1} suggests no more than a weak hydrogen bond. We have derived, and refined to $R = 0.073$, a structure based on space group *I*4/*m* in which the perchlorate group is satisfactorily tetrahedral and there is no unusual hydrogen bond. Since part of this structure is essentially different from the earlier $I\bar{4}$ structure, we describe it in some detail.

For the structure of the cation to be described in *I*4/*m*, the published coordinates of the Cd, S, C, and N atoms (Table

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Table II. Final $C2/c$ Parameters for $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru	0.30402 (5)	0.15268 (10)	−0.02163 (4)	2.55 (2)	3.10 (2)	3.04 (2)	−0.07 (3)	0.55 (2)	−0.19 (3)
O(1,7)	0.3055 (4)	0.3254 (9)	−0.1128 (3)	3.4 (2)	4.0 (3)	3.0 (2)	−0.4 (2)	0.7 (2)	0.0 (2)
O(2,8)	0.4088 (3)	0.3131 (8)	0.0356 (3)	2.9 (2)	3.8 (3)	3.7 (2)	−0.6 (2)	0.5 (2)	−0.2 (2)
O(3,5)	0.3014 (4)	−0.0166 (8)	0.0697 (3)	3.7 (2)	3.2 (3)	3.8 (3)	0.1 (2)	0.5 (2)	0.2 (2)
O(4,6)	0.1994 (4)	−0.0016 (8)	−0.0791 (3)	3.4 (2)	3.6 (3)	4.0 (3)	−0.4 (2)	0.4 (2)	−0.5 (2)
F(1,2)	−0.0701 (5)	0.7056 (13)	0.2146 (5)	9.0 (5)	9.4 (6)	12.0 (6)	1.6 (4)	−1.1 (4)	3.9 (5)
F(3,4)	−0.0352 (6)	0.4807 (13)	0.3003 (4)	12.2 (6)	11.3 (6)	8.0 (4)	0.9 (5)	4.2 (4)	4.7 (4)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(9,10)	0.4173 (4)	−0.0453 (10)	−0.0639 (4)	4.8 (1)	C(3,7)	0.3864 (6)	0.4561 (13)	0.0749 (5)	3.5 (2)
C(1,5)	0.2524 (6)	0.4725 (13)	−0.1195 (5)	3.5 (2)	C(4,8)	0.4625 (6)	0.5744 (14)	0.1178 (5)	4.4 (2)
C(2,6)	0.2543 (6)	0.6034 (14)	−0.1872 (5)	4.6 (2)	B	0.0	0.5970 (22)	0.25	3.9 (3)

[a] The form of the anisotropic B's is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)]$.

Table III. Bond Distances and Angles in $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$

	$C2/c$[a]	Cc[3]
	Distances (Å)	
Ru-Ru	2.248 (1)	2.248
Ru-O(1,7)	2.008 (5)	2.02, 2.01
Ru-O(2,8)	2.025 (5)	2.06, 1.97
Ru-O(3,5)	1.998 (6)	1.90, 2.05
Ru-O(4,6)	2.002 (6)	1.99, 2.02
Ru-O(9,10)	2.310 (6)	2.34, 2.27
C(1,5)-O(1,7)	1.264 (10)	1.16, 1.35
C(1,5)-O(3,5)	1.274 (10)	1.36, 1.21
C(3,7)-O(2,8)	1.270 (10)	1.34, 1.17
C(3,7)-O(4,6)	1.273 (10)	1.24, 1.28
C(1,5)-C(2,6)	1.502 (12)	1.54, 1.52
C(3,7)-C(4,8)	1.487 (13)	1.42, 1.57
B-F(1,2)	1.340 (17)	1.42, 1.30
B-F(3,4)	1.341 (17)	1.46, 1.38
	Angles (Deg)	
O(1,7)-Ru-O(2,8)	89.8 (2)	91.7, 87.3
O(1,7)-Ru-O(3,5)	179.2 (2)	179.3, 178.6
O(1,7)-Ru-O(4,6)	89.4 (2)	88.4, 90.7
O(2,8)-Ru-O(3,5)	90.2 (2)	88.9, 92.7
O(2,8)-Ru-O(4,6)	179.0 (2)	178.1, 174.2
O(3,5)-Ru-O(4,6)	90.6 (2)	91.0, 89.1
Ru-O(1,7)-C(1,5)	119.1 (5)	121, 117
Ru-O(3,5)-C(1,5)	119.6 (5)	115, 123
Ru-O(2,8)-C(3,7)	118.6 (5)	117, 124
Ru-O(4,6)-C(3,7)	119.9 (5)	125, 116
C(2,6)-C(1,5)-O(1,7)	119.2 (7)	130, 106
C(2,6)-C(1,5)-O(3,5)	118.7 (7)	105, 134
O(3,5)-C(1,5)-O(1,7)	122.1 (7)	124, 121
C(4,8)-C(3,7)-O(2,8)	119.3 (7)	114, 127
C(4,8)-C(3,7)-O(4,6)	118.6 (7)	127, 110
O(4,6)-C(3,7)-O(2,8)	122.2 (7)	119, 123
F(1,2)-B-F(1,2)	112.0 (12)	112
F(1,2)-B-F(3,4)	109.0 (12)	100, 111
F(1,2)-B-F(3,4)	110.1 (12)	89, 134
F(3,4)-B-F(3,4)	106.4 (11)	101

[a] This work.

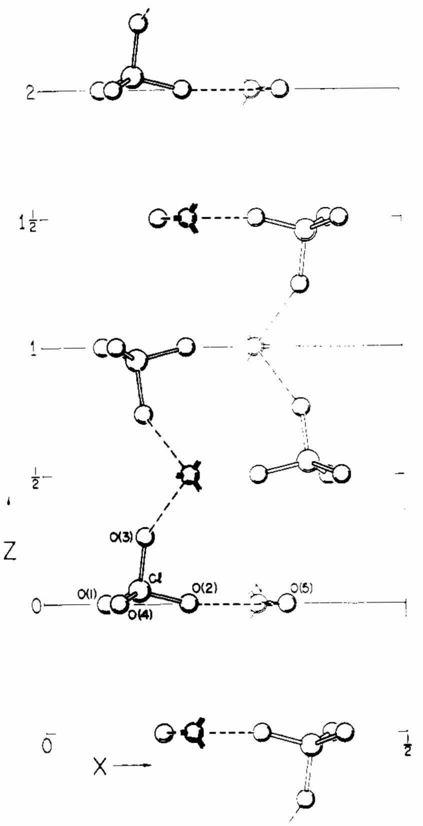

Figure 1. Proposed arrangement of ClO_4^- ions and water molecules O(5) in the structure of *catena*-bis[μ-(N-methylpiperidinium-4-thiolato)]-cadmium(II) perchlorate dihydrate.

II of ref 5) must be incremented by (0, $^1/_2$, $^1/_4$) so that the piperidine ring lies across the mirror plane at $z = 0$. The difference map based on this partial model gave clear indication of the ClO_4^- ion at approximately the position reported in ref 5; this is a disordered arrangement in $I4/m$, with three of the oxygen atoms lying approximately on the mirror plane and the fourth oxygen atom and the chlorine atom lying on one side or the other with equal probability. The peak associated with the water molecule, O(5), also lay on the mirror plane but was much weaker than would correspond to full occupancy, and a population parameter for this site was included in subsequent least-squares cycles. This model con-

Table IV. Final $I4/m$ Parameters for $Ru_2(O_2CC_2H_5)_4Cl$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru	0.0	0.0	0.1532 (6)	2.91 (3)	2.91	1.11 (6)	0.0	0.0	0.0
Cl	0.0	0.0	0.5	5.8 (2)	5.8	0.7 (5)	0.0	0.0	0.0
O(1,2)	0.1558 (6)	0.0944 (7)	0.1499 (14)	3.1 (3)	5.3 (4)	2.2 (3)	−1.0 (3)	−0.5 (4)	−0.4 (5)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.202 (2)	0.124 (2)	0.0	3.7 (4)	C(3)	0.414 (3)	0.145 (3)	0.084 (4)	5.6 (7)
C(2)	0.316 (2)	0.202 (2)	0.0	5.0 (5)					

[a] The form of the anisotropic B's is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)]$.

Table V. Bond Distances and Angles in $Ru_2(O_2CC_2H_5)_4Cl$

	$I4/m$[a]	$I\bar{4}$[3]
	Distances (Å)	
Ru-Ru′	2.274 (9)	2.292
Ru-Cl	2.575 (7)	2.566
Ru-O(1,2)	2.013 (7)	1.92, 2.04
O(1,2)-C(1)	1.27 (2)	1.22, 1.43
C(1)-C(2)	1.52 (3)	1.61
C(2)-C(3)	1.40 (4)	1.60
	Angles (Deg)	
Ru′-Ru-O(1,2)	89.3 (3)	95, 88
O(1,2)′-Ru-O(1,2)	178.6 (4)	171, 176
O(1,2)′-Ru-O(1,2)″	90.0 (1)	88, 92
Ru-O(1,2)-C(1)	119.5 (10)	117, 113
O(1,2)′-C(1)-O(1,2)	122.4 (16)	127
O(1,2)′-C(1)-C(2)	118.8 (16)	134, 100
C(1)-C(2)-C(3)	112.3 (20)	119

[a] This work.

verged, in two cycles, at $R = 0.076$; the population parameter of O(5) was 0.43 (3).

A three-dimensional difference map calculated at this stage indicated a diffuse column of residual electron density along the line $x = 0$, $y = 0$, with a maximum value of about 1.0 e/Å^3 near $z = 0.2$; a projection of the map onto (001) showed a clear peak of height 3.9 e/Å^3. It seemed apparent that additional water is present, occupying this otherwise empty region of the structure; this water is represented as O(6).

Our final model was based on 82 atomic parameters, including population parameters for the two water sites O(5) and O(6); see Table VI. Isotropic B's were assigned to the chlorine atom, which lies close to the mirror plane and hence would show large correlation between position and anisotropy, and to the additional water molecule O(6); all other atoms were treated anisotropically, as in ref 4. Our final R was 0.073, compared to $R = 0.076$ for 130 parameters in the $I\bar{4}$ model. A final difference map showed features reaching 1.0 e/Å^3 at the Cd site, probably reflecting small systematic errors from absorption or such, but nothing else above 0.6 e/Å^3; the projected difference density was similarly uninteresting.

Both the piperidinium ion and the ClO_4^- ion structures (Table VII) are very remarkably more satisfactory than before. The values for the ClO_4^- group are of much less significance than indicated by their formal esd's, however, since O(1), O(2), and O(4) were placed on a mirror plane and hence cannot be distinguished from their partners in disorder. The most significant change in the structure involves the water molecule O(5), which we find to occupy its site only half (0.50 ± 0.03) the time. As a result, there need be no short hydrogen bond as was required by the $I\bar{4}$ structure. We envisage chains of ClO_4^- ions and H_2O molecules with composition $(ClO_4^-)_2 \cdot H_2O$ and an effectively doubled c axis, as shown in Figure 1. Each water molecule O(5) makes a relatively weak (3.06 (3) Å) hydrogen bond to O(2) of a neighboring chain and accepts a hydrogen bond from an ammonium group (N···O = 2.76 (2) Å); half the ammonium groups, however, have no adjacent O(5) but instead bond to one or both of two neighboring O(3) atoms at 3.08 (3) Å. Long-range disorder in the chains evidently then halves c back to its original value. (It seems possible, though, that there may be enough order within these arrays to be evidenced by weak, diffuse odd-order layer lines on rotation photographs about c.)

The additional water, O(6), has a site population factor of 0.60 (5). It occupies a large cavity in the structure, with nearest neighbors O(4) at 3.37 (7) Å and, at least part of the time, another O(6) at 2.60 (12) Å. The total amount of water,

Table VI. Final $I4/m$ Parameters for *catena*-Bis[μ-(N-methylpiperidinium-4-thiolato)]-cadmium(II) Perchlorate Dihydrate[a]

atom	x	y	z	N	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd(1,2)	0	0.5	0.25	4	32.8 (1)	32.8	207 (3)	0	0	0
S	0.1024 (1)	0.5092 (1)	0	8	25 (1)	31 (1)	268 (7)	0 (1)	0	0
C(1)	0.1393 (6)	0.4171 (6)	0	8	32 (4)	32 (4)	408 (41)	4 (3)	0	0
C(2,5)	0.1842 (5)	0.4054 (5)	0.187 (2)	16	44 (3)	59 (4)	399 (31)	12 (3)	7 (9)	39 (10)
C(3,4)	0.2526 (5)	0.4506 (5)	0.185 (2)	16	43 (3)	61 (4)	352 (28)	10 (3)	−27 (8)	−20 (9)
C(6)	0.3638 (8)	0.4763 (8)	0	8	34 (5)	47 (6)	1114 (106)	−6 (4)	0	0
N	0.2955 (5)	0.4344 (6)	0	8	31 (3)	44 (4)	508 (41)	1 (3)	0	0
Cl	0.1315 (2)	0.1925 (3)	0.0511 (8)	8	B(iso) = 6.76 (12) Å^2					
O(1)	0.0856 (6)	0.2503 (6)	0	8	65 (5)	56 (4)	728 (53)	16 (4)	0	0
O(2)	0.1995 (7)	0.2036 (10)	0	8	53 (5)	117 (10)	1389 (105)	9 (6)	0	0
O(3)	0.1410 (12)	0.1912 (12)	0.261 (4)	8	103 (11)	113 (12)	699 (86)	58 (10)	70 (29)	53 (30)
O(4)	0.1042 (10)	0.1291 (7)	0	8	135 (11)	60 (6)	959 (76)	−23 (6)	0	0
O(5)	0.3360 (13)	0.2930 (11)	0	4.0 (2)	74 (11)	39 (7)	564 (103)	11 (7)	0	0
O(6)	0	0	0.195 (10)	2.4 (2)	B(iso) = 26 (3) Å^2					

[a] The form of the anisotropic B's is $10^4 \exp(-B_{11}h^2 - \ldots - 2B_{23}kl)$.

Table VII. Bond Distances and Angles for *catena*-Bis[μ-(N-methylpiperidinium-4-thiolato)]-cadmium(II) Perchlorate Dihydrate

bond	value, Å		angle	value, deg	
	this work	ref 4		this work	ref 4
Cd-S	2.548 (2)	2.546, 2.550	Cd-Cd-S	49.2	49.1, 49.3
S-C(1)	1.861 (12)	1.85	Cd-S-Cd	81.6	81.6
C(1)-C(2,5)	1.519 (13)	1.48, 1.56	Cd-S-C(1)	102.6 (4)	102, 103
C(2,5)-C(3,4)	1.539 (14)	1.44, 1.67	S-C(1)-C(2,5)	109.9 (7)	108, 113
C(3,4)-N	1.505 (11)	1.44, 1.61	C(1)-C(2,5)-C(3,4)	112.2 (8)	120, 105
N-C(6)	1.503 (18)	1.55	C(2,5)-C(3,4)-N	109.9 (8)	109, 105
Cl-O(1)	1.425 (13)	1.35	C(3,4)-N-C(3,4)	110.3 (9)	110
Cl-O(2)	1.337 (15)	1.27	C(3,4)-N-C(6)	110.5 (9)	105, 115
Cl-O(3)	1.411 (25)	1.44	C(2,5)-C(1)-C(2,5)	110.1 (10)	(108)
Cl-O(4)	1.339 (17)	1.30	O(1)-Cl-O(2)	113.4 (9)	120
N···O(5)	2.76 (2)	2.79	O(1)-Cl-O(3)	109.1 (11)	100
N···O(3)	3.08 (3)		O(1)-Cl-O(4)	112.6 (9)	118
O(5)···O(2)	3.06 (3)	3.18	O(2)-Cl-O(3)	97.7 (12)	82
O(6)···O(4)	3.37 (7)		O(2)-Cl-O(4)	116.0 (10)	121
O(6)···O(6)	2.60 (12)		O(3)-Cl-O(4)	106.5 (12)	94

then, is 6.4 (3) molecules per cell, appreciably less than the eight that would correspond to the reported dihydrate.[5] The water content was determined by thermal gravimetric analysis,[5] which indicated the loss of 1 mol of water between 40 and 85 °C and a second mole between 85 and 120 °C (no error estimate is given). It seems likely that the weakly bound water, O(6), is lost at the lower temperature, and some of this water may have been lost before or during data collection. We note that the density calculated for 6.4 molecules of water per cell is in exact agreement with the measured density of 1.70 g cm^{-3} whereas the value calculated for eight molecules per cell is somewhat higher at 1.725 g cm^{-3}.

Registry No. **2**, 71106-46-2; **4**, 71106-47-3; *catena*-bis[μ-(*N*-methylpiperidinium-4-thiolato)]-cadmium(II) perchlorate dihydrate, 71359-32-5; $Nb_2Br_6(SC_4H_8)_3$, 38531-74-7; $Ta_2Br_6(SC_4H_8)_3$, 65651-12-9.

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[6] Contribution No. 6266.

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Received July 29, 1980

A Fourier-Transform NMR Investigation of $[(C_4H_9)_4Z][MP(C_6H_5)_3I_3]$ (Z = N, P; M = Co, Ni)

Sir:

The nature of the interactions within ion couples of the type $(R_4Z)_n{}^+ML_m{}^{n-}$ in aprotic solvents has been extensively investigated through ^1H isotropic shift techniques in paramagnetic compounds.[1,2] Detailed models were proposed for the interactions between $(n\text{-}C_4H_9)_4N^+$ (Bu_4N^+ hereafter) and several paramagnetic anionic complexes.[3-5]

The models were based on the assumption that the observed isotropic shifts (i.e., the difference between the chemical shift of the paramagnetic compound and the chemical shift of the analogous diamagnetic compound) for the protons in the cation were primarily dipolar.[4-6] However, Burkert et al.[7] and Brown and Drago[8] reported evidence of predominant contact contributions on the nitrogen of Bu_4N^+ through ^{14}N NMR spectroscopy. An analogous conclusion had been reached by comparing the ^{31}P and the ^1H shifts of Bu_4P^+ in the same kind of complexes.[9]

The dipolar interactions arise from through-space coupling between nuclei and unpaired electrons; the effectiveness of such a mechanism is linked to the magnetic anisotropy of the paramagnetic complex and is strongly dependent on geometrical parameters. The contact shift is present whenever there is unpaired spin density on s orbitals of the nucleus under consideration; it is generally believed to be negligible in the absence of true chemical bond. The separation of the above contributions is not straightforward especially in the absence of independent structural and magnetic data.[10,11] An attempt to separate contact and dipolar contributions in ion-pair systems is also reported.[12]

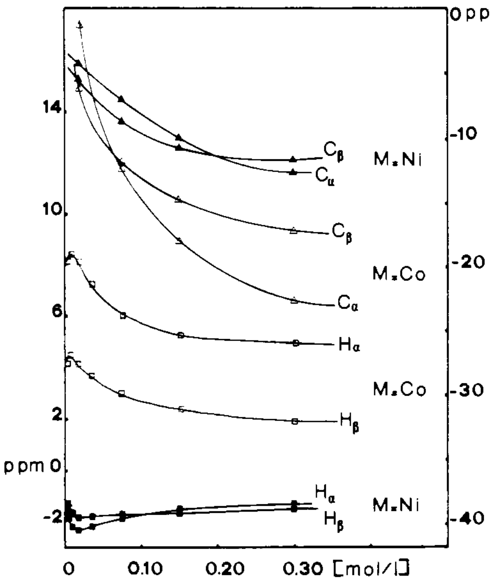

Figure 1. Isotropic shifts of some cation nuclei in $[(n\text{-}C_4H_9)_4N][MP(C_6H_5)_3I_3]$ = Co, Ni) as a function of complex concentrations. The isotropic shift scale is on the left for ^1H and on the right for ^{13}C.

We thought to reinvestigate ion-couple systems through FT NMR techniques which allow for the measurement of NMR parameters of ^{13}C in natural abundance as well as the relaxation rates of the various cation nuclei. The relaxation mechanisms contain a contribution due to electron–nucleus coupling occurring through a contact and a dipolar interaction whose separation is often easier to accomplish.[13] Comprehension and comparison of the NMR parameters of the various nuclei may allow a deeper insight into the problem of the nature of the interactions within ion couples.

After this research was completed, a paper appeared[14] dealing with the isotropic shifts of hydrogen and carbon nuclei of Bu_4N^+ in melted salts of the type $(Bu_4N)_2MBr_4$ (M = Mn, Co, Ni). By comparison between the ^1H and ^{13}C shifts the authors concluded that the dipolar contributions to the overall isotropic shifts were negligible. However, they found their data highly temperature dependent, in such a way that they could not establish the meaning of their observations with respect to dilute solutions.

We wish to report here the isotropic shifts and the relaxation rates of the complexes $(Bu_4Z)MPPh_3I_3$, where Z = N, P and M = Co, Ni, as well as the ^1H and ^{13}C isotropic shifts for the complexes $(Bu_4N)_2MX_4$, where M = Co, Ni and X = Br, I. Such values are referred to the diamagnetic zinc analogues.

The isotropic shifts for the above complexes are reported in Table I. The values refer to 0.3 M concentration. The sign and magnitudes of the ^1H shifts agree with the values previously reported,[15] if some allowance is made for the different concentrations (see below). In the case of the tetrabromo complexes, the shifts of the protons are upfield for

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