Notes

Composition and Structure of a Co(en)$_2$Cl(benzimidazole) Salt

Richard E. Marsh

Division of Chemistry and Chemical Engineering,† Beckman Institute, California Institute of Technology, Pasadena, California 91125

Received May 8, 1992

Introduction

I wish to make a number of corrections to the description of the composition and crystal structure of a compound previously identified as "bis(ethylenediamine)(benzimidazole)chlorocobalt(III) perchlorate".[1] The corrections are as follows: (1) the compound is the chloride salt, rather than the perchlorate; (2) the crystals are hydrated, with the empirical formula being approximately [Co(en)$_2$(Cl)(benzimidazole)]Cl$_2$·1.3H$_2$O; (3) the calculated density is 1.56, rather than 2.94, g/cm^3; (4) the crystals are monoclinic, space group $C2/c$, rather than triclinic, $P\bar{1}$.

Experimental Section

The lattice vectors $(1\bar{2}0)$, $(\bar{1}00)$, and $(01\bar{1})$ in the original, triclinic representation[1] describe a C-centered cell with a = 21.638 Å, b = 8.168 Å, c = 22.083 Å, α = 90.04°, β = 111.30°, and γ = 89.91°. When the indices of the 3437 F_o values in the supplementary material[2] were transformed as above and the F_o's were averaged according to Laue symmetry $2/m$, the value of R_{merge} was 0.023 for 1207 duplicates; none of the reflections was of the type $h0l$ with l odd that is forbidden by $C2/c$. Least-squares refinement began with the triclinic coordinates,[1] suitably transformed and averaged. Subsequent difference maps showed the presence of water molecules, but no indication of perchlorate oxygen atoms. Hydrogen atoms of the cation were placed in calculated positions, and not refined; those of the water molecules were ignored. The final R was 0.044 for 2229 reflections, compared with 0.067 for the earlier, triclinic description.[1] Final coordinates are given in Table I.

Results and Discussion

The water molecules are involved in an interesting type of disorder. W2 (Table I) is present only about 30% of the time; its presence causes W1 to move from its preferred site W1A to W1B in order to avoid a very short (2.05 Å) W1- -W2 distance. Then, as a further consequence, one en group inverts its conformation so as to allow a more reasonable N(21)- -W1B hydrogen bond. The three population parameters—those of W2, of the minor component W1B, and of the minor en conformer C21B–C22B—were originally refined separately, and all converged to essentially the same value; at the end, they were combined into a single parameter.

Table I. Coordinates in Space Group $C2/c$ (x, y, z and $U_{eq} \times 10^4$)

atom	x	y	z	U_{eq} or B^c
Co	3584 (0.3)	5423 (0.7)	4148 (0.3)	287 (1)
Cl	4585 (1)	6408 (2)	4202 (1)	453 (3)
Cl1	1812 (1)	3970 (2)	2479 (1)	627 (4)
Cl2	2921 (1)	915 (1)	4641 (1)	497 (3)
N1	3813 (2)	5725 (4)	5086 (2)	336 (9)
C2	3715 (2)	4595 (6)	5469 (2)	380 (10)
N3	3924 (2)	5065 (5)	6096 (2)	423 (10)
C9	4179 (2)	6615 (6)	6129 (3)	392 (11)
C4	4438 (3)	7675 (8)	6658 (3)	575 (16)
C5	4648 (3)	9171 (8)	6526 (4)	732 (18)
C6	4596 (3)	9601 (7)	5904 (3)	641 (15)
C7	4335 (2)	8553 (6)	5383 (3)	507 (13)
C8	4119 (2)	7039 (5)	5502 (2)	351 (10)
N11	2695 (2)	4683 (4)	4064 (2)	339 (8)
C11	2281 (2)	6124 (6)	4076 (3)	427 (12)
C12	2438 (2)	7416 (6)	3672 (3)	413 (11)
N12	3172 (2)	7593 (4)	3927 (2)	334 (8)
N21	3392 (2)	4990 (4)	3225 (2)	409 (9)
N22	3952 (2)	3193 (5)	4287 (2)	380 (9)
C21A[a]	3792 (4)	3601 (10)	3142 (5)	3.9 (2)*
C21B[b]	3523 (11)	3182 (25)	3170 (12)	4.6 (4)*
C22A[a]	3747 (4)	2335 (10)	3631 (5)	3.7 (2)*
C22B[b]	4042 (9)	2631 (20)	3725 (10)	3.3 (3)*
W1A[a]	814 (4)	1579 (10)	2715 (5)	8.8 (3)*
W1B[b]	399 (8)	2090 (19)	2294 (9)	6.5 (4)*
W2[b]	1808 (7)	1154 (18)	3242 (9)	6.9 (5)*

[a] Population: 0.694 (9). [b] Population: 0.306. [c] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j[U_{ij}(a_ia_j)(\bar{a}_i\bar{a}_j)]$. An asterisk denotes the isotropic displacement parameter, B.

The absence of perchlorate in these crystals is clearly demonstrated not only by the failure of the oxygen atoms to appear in difference maps but also by the many strong hydrogen bonds accepted by the Cl$^-$ ions—five by Cl1 and four by Cl2; there is no room for oxygen atoms. Professor Raymond Butcher (private communication) confirms that the compound was indeed the chloride salt, the confusion being caused by a mislabeled bottle. There are no appreciable changes in the bond lengths previously reported,[1] with the possible exception that all five Co–N bond lengths are now identical within their esd's, at 1.963 (2) Å.

While the revised density of 1.56 g/cm^3 is reasonable, the earlier value of 2.94 g/cm^3 was not; it was apparently calculated on the basis of eight (unhydrated) molecules per triclinic cell rather than four.

The original paper[1] also reported the structure of [Co(en)$_2$(py)Cl]Cl$_2$, crystallized by vapor diffusion of ethanol into a dilute solution of the compound. Dr. Butcher (private communication) notes that a reference[3] to a structure determination of the corresponding hydrate, [Co(en)$_2$(py)Cl]Cl$_2$·H$_2$O, was not included. There are no statistically significant differences between the bond lengths in the two crystal forms, both of which crystallized as racemates.

† Contribution No. 8627.

(1) Rowan-Gordon, N.; Nguyenpho, A. A.; Mondon-Konan, E.; Turner, A. H.; Butcher, R. J.; Okonkwo, A. S.; Hayden, H. H.; Storm, C. B. *Inorg. Chem.* **1991**, *30*, 4374.

(2) Approximately one-third of the available reflections were apparently not collected—those with k and l having opposite signs (in the triclinic description). After the transformation and averaging, perhaps 20% of the possible reflections were missing from the monoclinic data set.

(3) Harrowfield, J. McB.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Aust. J. Chem.* **1986**, *39*, 339. (The method by which the crystals were grown was not mentioned in this paper.)

0020-1669/92/1331-4890$03.00/0