

THE STRUCTURAL *TRANS* EFFECT. A REFINEMENT OF THE CRYSTAL STRUCTURE OF CARBONATOTETRAAMMINECOBALT(III) BROMIDE

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The structure of carbonatotetraamminecobalt(III) bromide reported¹ by Barclay and Hoskins has a significant lengthening of the Co-NH₃ bond *trans* to the carbonate group. While this result was not prominently stated in this report a subsequent review² does so and concludes that the carbonate ion give rise to a significant structural *trans* effect in cobalt(III) complexes. The recently determined structure³ of *cis*-carbonatobis(1,3-diaminopropane)cobalt(III) perchlorate, [Co(tn)₂CO₃][ClO₄], does not exhibit this effect. This result and the fact that the former structure had been refined only by Fourier methods suggested that a full-matrix least-squares refinement using the original data may show the effect to be a refinement artefact. Few structures with coordinated carbonate have been determined. The only other one known is that of a cobalt(II) complex.⁴ In the course of their analysis of a coordinated nitrate, Cotton and Soderberg⁵ carried out a re-refinement and reported with no details that their atomic positions would not give bond lengths differing by more than 0.01 Å from those of Barclay and Hoskins.¹ The results given below are not in agreement with this conclusion and it was thought worthwhile in view of the interest in the structural *trans* effect to report them in full.

Refinement

The unit-cell† and intensity data (458 non-zero, visually estimated reflections collected by the Weissenberg technique using Co-K α radiation) of Barclay and Hoskins¹ were used. The refinement‡ was started with their atomic coordinates and

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† Orthorhombic, space group P_{cmn} , a 6.760(5) Å, b 7.629(5) Å, c 16.886(10) Å, Z 4.

‡ Refinement carried out with the program FUORFLS (a modification of ORFLS by M. R. Taylor) and The University of Adelaide CDC6400 computer. Source of atomic scattering factors: Co²⁺ and Br⁻, Doyle, P. A., and Turner, P. S., *Acta crystallogr. (A)*, 1968, **24**, 390; O, N, C, "International Tables for X-ray Crystallography." Vol. III, p. 202. (Kynoch Press: Birmingham 1962.)

¹ Barclay, G. A., and Hoskins, B. F., *J. chem. Soc.*, 1962, 586.

² Pratt, J. M., *Adv. inorg. Chem. Radiochem.*, 1969, **12**, 375.

³ Geue, R. J., and Snow, M. R., *J. chem. Soc. (A)*, 1971, 2981.

⁴ Baraniak, E., Freeman, H. C., James, J. M., and Nockolds, C. E., *J. chem. Soc. (A)*, 1970, 2558.

⁵ Cotton, F. A., and Soderberg, R. H., *J. Am. chem. Soc.*, 1963, **85**, 2402, footnote 24.

estimated values of the isotropic thermal parameters. Isotropic temperature factors have been used for the refinement; the limited extent and quality of the data does not appear to warrant anisotropic temperature factors. Individual scale factors were assigned to the original Weissenberg levels $0kl$ and $h0l \rightarrow h4l$. At convergence, no scale factor differed from the mean scale factor by more than 1.5σ ; this indicates that the original scaling was satisfactory. Three cycles of refinement were carried out with unit weights to establish a weighting scheme. The discrepancies* Δ^2 were plotted in ranges of F_0 . A Hughes weighting scheme, $w = 1/(4.5 + F_0)$, was chosen so that the function $w\Delta^2$ had no systematic trend with F_0 . The refinement converged in three

TABLE 1

FINAL ATOMIC PARAMETERS FOR $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Br}$

Estimated standard deviations are given here and elsewhere in parentheses. Where no estimate is given, the parameter is fixed by crystallographic symmetry

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> (Å ²) |
|------|-------------|------------|------------|----------------------------|
| Br | 0.5415(4) | 0.25 | 0.2760(2) | 3.1(1) |
| Co | 0.1184(5) | 0.25 | 0.0905(2) | 2.2(1) |
| O 1 | -0.3743(29) | 0.25 | 0.0163(11) | 3.1(4) |
| O 2 | -0.1062(15) | 0.1042(23) | 0.0641(6) | 2.3(2) |
| N 1 | 0.0361(36) | 0.25 | 0.2027(17) | 3.7(5) |
| N 2 | 0.3075(32) | 0.25 | 0.4802(11) | 2.5(4) |
| N 3 | 0.3057(23) | 0.0577(24) | 0.1120(9) | 3.0(3) |
| C | -0.2063(38) | 0.25 | 0.0452(14) | 2.3(5) |

TABLE 2

COMPARISON OF BOND-LENGTHS (Å) AND ANGLES (°)

| Bond | Ref. 1 | This work | Angle | Ref. 1 | This work |
|--------|--------|-----------|-------------|--------|------------|
| Co-N 1 | 1.95 | 1.98(2) | N 1-Co-N 3 | 92.8 | 90.2(8) |
| Co-N 2 | 1.93 | 1.93(2) | N 2-Co-N 3 | 89.3 | 90.6(8) |
| Co-N 3 | 2.03 | 1.97(2) | N 3-Co-N 3 | 94.3 | 96.1(1.0) |
| Co-O 2 | 1.91 | 1.93(1) | N 1-Co-O 2 | 88.9 | 90.0(6) |
| C-O 1 | 1.24 | 1.24(4) | N 2-Co-O 2 | 89.5 | 89.0(6) |
| C-O 2 | 1.34 | 1.34(3) | O 2-Co-O 2' | 70.5 | 70.5(6) |
| | | | O 2-Co-N 3 | 97.7 | 96.8(7) |
| | | | O 2-C-O 1 | 124.8 | 123.9(1.5) |
| | | | O 2-C-O 2' | 110.4 | 112.7(1.4) |
| | | | C-O 2-Co | 89.5 | 88.5(8) |

further cycles. The average value of $w\Delta^2$ remained reasonably constant as a function of F_0 and had values in the range 0.7 ± 0.3 . This result and a standard deviation of a reflection of unit weight $[= \Sigma w\Delta^2/(n-m)]$, where $n-m$ is the excess of observation over parameters refined] with a value near unity (0.87) confirm that the weighting scheme is satisfactory. The final value of R_1 was 0.109 showing improvement over the original refinement¹ (0.12). The value of R_2 was 0.15. Table 1 lists the final atomic parameters and Table 2 compares the molecular geometry calculated from

* F_o and F_c are the observed and calculated structure factors,

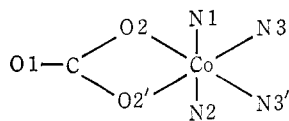
$$\Delta = F_o - F_c, R_1 = \Sigma |F_o - F_c| / \Sigma |F_o|, R_2 = (\Sigma \Delta^2 / \Sigma F_o^2)^{1/2}$$

$w (= 1/\sigma^2)$ is its expected standard deviation. The function minimized in least squares was $\Sigma w\Delta^2$.

them with those obtained previously.¹ The figure shows the atomic numbering; dashed and corresponding undashed atoms are related by crystallographic mirror symmetry. The mirror lies in the O 1, C, Co, N 1, N 2 plane.

Discussion

In general the detail of the molecular geometry agrees closely with the earlier refinement. The bond angles agree to within 2° and the bond lengths agree within



0.03 Å except in the case of Co-N3 which has contracted by 0.06 Å on re-refinement. The Co-NH₃ bond lengths average 1.96 Å in good agreement with those found in hexaammine and pentaammine complexes ([Co(NH₃)₆]I₃,⁶ 1.96 Å; [Co(NH₃)₅Cl]Cl₂,⁷ 1.97 Å). This mean is also the

same as that found in the structure³ of [Co(tn)₂CO₃]ClO₄, where the range of the non-equivalent Co-N bonds was 1.94(2) to 1.97(2) Å. The conclusion that Co-N3 is significantly lengthened in [Co(NH₃)₄CO₃]Br is not substantiated and both carbonate structures show that carbonate does not give rise to a structural *trans* effect above the 0.02 Å level. The carbonate ion can therefore be added to a growing list of anions including nitro,⁸ chloro,⁷ thiosulphate,⁹ and thiocyanato¹⁰ (both sulphur ligands are sulphur-bonded) which do not show the effect in ammine cobalt(III) complexes. Nitrosyl (formally NO⁻) does, however, show a large effect.¹¹

The observation of Cotton and Soderberg⁵ that their re-refinement showed no differences in bond lengths exceeding 0.01 Å from the original structure is generally confirmed for the cobalt-carbonate part of the complex, the region in which they were interested. The molecular geometry³ of the carbonate in [Co(tn)₂CO₃]ClO₄ is also in good agreement with that in the tetraammine structure.

Acknowledgments

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⁶ Barnet, M. T., Craven, B. M., Freeman, H. C., Kine, N. E., and Ibers, J. A., *Chem. Commun.*, 1966, 307.

⁷ Messmer, G. G., and Amma, E. L., *Acta crystallogr. (B)*, 1968, **24**, 417.

⁸ Cotton, F. A., and Edwards, W. T., *Acta crystallogr. (B)*, 1968, **24**, 474.

⁹ Baggio, S., *J. chem. Soc. (A)*, 1970, 2384.

¹⁰ Snow, M. R., and Boomsma, R. F., *Acta crystallogr.*, 1972, in press.

¹¹ Pratt, C. S., Coyle, B. A., and Ibers, J. A., *J. chem. Soc. (A)*, 1971, 2146.