rium, the monomer solution in B was poured into A by inclining the apparatus. The polymerization temperature was changed rapidly, if required, by transferring the apparatus to another bath and shaking it vigorously. The temperature was recorded by means of a thermocouple inserted in another apparatus in the same condition.

After polymerization was stopped by adding methanol, polymer was precipitated with petroleum ether, dissolved in acetone, precipitated again with 8% hydrochloric acid, washed with water, and then dried under vacuum at 50° for 24 hr. The yield was about 60 and 80% in the low temperature polymerizations for 6 hr initiated with PhMgBr and Ph_2Mg, respectively. The yield decreased at higher temperatures.

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The Molecular Structure of a Peroxo-Bridged Dicobalt Cation

Sir:

There exists a large number of compounds containing two cobalt atoms connected by one, two, or three bridging groups. These bridging groups include hydroxo, amido, peroxo, and nitrito radicals; the remaining coordination sites on the cobalt atoms can be occupied by ammine groups, cyanide ions, or organic amines. The nature of the bonding in these bridged compounds, and especially in those containing peroxo and nitrito bridges, has been the subject of discussion since their discovery. We have now determined by single crystal X-ray diffraction techniques the structure of a sulfate of the cation $[(NH_3)_5CoO_2Co(NH_3)_5]^{+5}$.

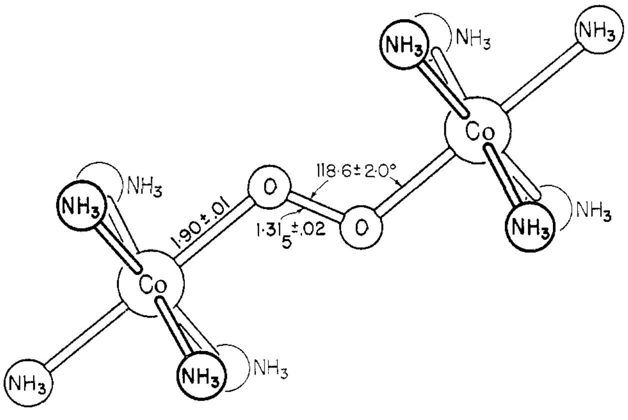

Figure 1. The geometry of the $[(NH_3)_5CoO_2Co(NH_3)_5]^{+5}$ cation.

The decaammine-μ-peroxodicobalt cation exists in an oxidized and a reduced form, the oxidized form (charge +5) being green and paramagnetic and the reduced form (charge +4) brown and diamagnetic. If the bridging group in the oxidized form is taken to be a peroxide ion, O_2^{-2}, then the cobalt atoms must have formal oxidation states +4 and +3 (or some other combination giving +7) to account for the +5 charge; alternatively, one can consider the bridging group to be a superoxide ion, O_2^{-}, and then both cobalt atoms can be in a more usual +3 oxidation state. Attempts have been made to decide between these two possibilities on the basis of the epr spectrum of the compound,[1] but these experiments have only demonstrated the equivalence of the cobalt atoms and have not provided information as to the distribution of electrons in the compound.

Goodman, Hecht, and Weil[2] have summarized these and other explanations and theories regarding the peroxo bridge in these types of compounds. The latest theoretical work is that of Vlček,[3] in which he considered the oxygen–oxygen bond to be perpendicular to the cobalt–cobalt axis; he presumed the bonding to be between d orbitals of the cobalt atoms and π electrons on the peroxo group, in analogy to the bonding in the platinum–olefin complexes. This structure was in fact subsequently reported by Vannerberg and Brosset[4] for the compound decaammine-μ-peroxodicobalt pentanitrate. However, their structure determination was based on only 234 observed reflections and the structure was refined only to an R factor of 19%; moreover, there was some question in their paper as to the correct space group, and they were forced to assume a disordered structure to obtain even the agreement they reported. Thus, their apparent confirmation of Vlček's structure is not reliable. Because of the unusual nature of the bonding postulated by Vlček and the importance of compounds such as this in constructing theories of bonding, we have examined the crystal structure of a different compound containing the same cation, decaammine-μ-peroxodicobalt monosulfate tris(bisulfate), $(NH_3)_5CoO_2Co(NH_3)_5SO_4(HSO_4)_3$. This is a new compound not previously reported; Vortmann[5] in his original paper on these compounds reported for the sulfate the formula $(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2HSO_4 \cdot 3H_2O$. This last compound forms when crystallization is from 1 F sulfuric acid; it is monoclinic and its structure is now under investigation in these laboratories.

The compound described here is obtained by crystallization from sulfuric acid more concentrated than about 2 F. It crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions a = 16.36, b = 13.95, and c = 9.98 A; there are four formula units in the cell. The structure was solved by Patterson methods and refined by three-dimensional least-squares methods based on 1458 reflections, with a final R factor of 0.077. Many features of this structure are of interest and these will be presented in detail elsewhere; the important information to be reported here is the molecular structure of the bridged peroxodicobalt cation, which is as shown in Figure 1. Each of the cobalt atoms is surrounded by five ammonia molecules and an oxygen atom of the bridging group. These are arranged at the corners of an almost regular octahedron, the cobalt–nitrogen distances all being 1.95 ±

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[1] I. Bernal, E. A. V. Ebsworth, and J. A. Weil, *Proc. Chem. Soc.*, 57 (1959).

[2] G. L. Goodman, H. G. Hecht, and J. A. Weil, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 90.

[3] A. A. Vlček, *Trans. Faraday Soc.*, **56**, 1137 (1960).

[4] N.-G. Vannerberg and C. Brosset, *Acta Cryst.*, **16**, 247 (1963).

[5] G. Vortmann, *Monatsh. Chem.*, **6**, 404 (1885).

0.02 A and the average deviation of a ligand–cobalt–ligand angle from 90° being less than 2°. The bridging peroxo group is *not* perpendicular to the cobalt–cobalt axis and is *not* joined to the metal atoms by d–π bonds, but each of the oxygen atoms is σ-bonded to one of the cobalt atoms, resulting in the staggered arrangement shown. These four atoms are almost coplanar; thus, in contrast to hydrogen peroxide, there is only a small dihedral angle at the oxygen–oxygen bond. This configuration probably arises because the ammonia molecules close to the bridge tend to keep the cobalt atoms as far apart as possible. The cobalt–cobalt distance, 4.56 A, is comparable to that reported by Vannerberg and Brosset[4] (4.52 A), but the oxygen–oxygen distance is signficantly shorter than theirs (1.31 *vs.* 1.45 A). The oxygen–oxygen distance we find is only slightly longer than that found in alkali metal superoxides, 1.28 A, and is much shorter than the 1.48 A found for most peroxides.[6] It is therefore reasonable to state that the bridging group is more nearly a superoxide radical and to expect that suitable epr measurements may show that the unpaired electron is found more on the oxygen atoms than on the cobalt atoms.

There seems to be no reason to believe that the geometry of the $[(NH_3)_5CoO_2Co(NH_3)_5]^{+5}$ cation should be different in the sulfate and the nitrate. Therefore, in view of the doubts mentioned earlier concerning the validity of Vannerberg and Brosset's structure analysis, we conclude that the structure reported here, rather than that postulated by Vlček, is generally correct for all such compounds.

(6) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 351, 352.

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Preparation of Elemental Carbon-13 in High Yield from $C^{13}O_2$

Sir:

Recent experimental work in this laboratory has resulted in the separation of highly enriched carbon-13 (natural abundance 1.1%) by the thermal diffusion of methane.[1] It was desired that elemental carbon be prepared from a portion of the separated $C^{13}H_4$. The separation of $C^{13}H_4$ is difficult, and the quantities of separated material are very limited; hence, a conversion procedure which would give a high yield was sought. Procedures for the conversion of methane to carbon dioxide or to barium carbonate are quantitative and straightforward; hence, any of these three compounds is satisfactory as a starting material.

Exploratory experiments on direct pyrolysis of methane gave unsatisfactory yields. Published work[2] on the preparation of carbon by fusion of barium carbonate with alkali metals or magnesium indicated that this procedure would also result in poor yields and possibly high contents of refractory impurities. This communication describes a method by which elemental carbon can be prepared from carbon dioxide in high yield and high purity.

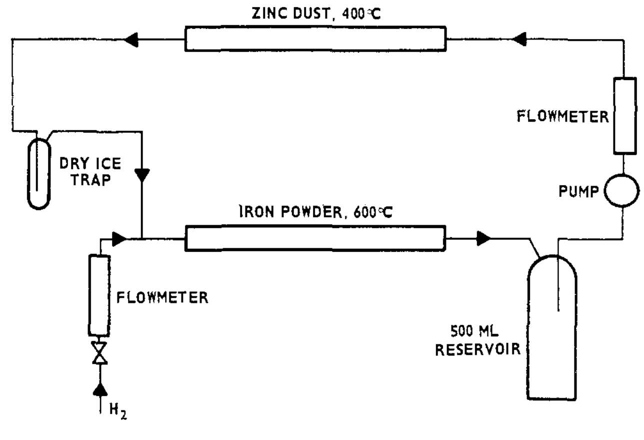

Figure 1. Apparatus for converting carbon dioxide to carbon.

The method is based on two well-known reactions: (1) the reduction of CO_2 to CO by zinc and (2) the reduction of CO over an iron catalyst in the presence of hydrogen.[3] The necessary apparatus is depicted schematically in Figure 1. Two quartz reaction tubes (12 mm i.d. × 50 cm long) are connected in a loop with a circulating pump,[4] a gas reservoir, and a Dry Ice cold trap. In the upper reactor CO_2 is reduced to CO over a 10-g charge of zinc dust. In the lower reactor carbon is formed on 20 mg of powdered iron catalyst *via* the reactions

$$2CO \longrightarrow C + CO_2$$

$$CO + H_2 \longrightarrow C + H_2O$$

The hydrogen content of the circulating gas is maintained at the desired level by continuous addition through a metering valve and a flow meter. The Dry Ice trap removes water formed in the second of the above reactions and also water resulting from reduction of zinc oxide in the upper reactor. When the process is complete, essentially all of the carbon in the starting CO_2 is deposited in the lower reactor, and the oxygen is collected as water in the Dry Ice trap. (Although a quantitative evaluation was not made, it appears that this procedure may also be useful for extracting oxygen isotopes from CO or CO_2.)

The apparatus is charged with CO_2 to an initial pressure of 500 to 600 torr (500 to 600 STP ml of gas in this system). The upper reactor is brought to 400°, and the reduction to CO is allowed to proceed for approximately 0.5 hr as the gas is circulated at a rate of 200–400 cc/min. The lower reactor is then heated to 600°, and the pressure is raised to 800 torr by the addition of hydrogen. After an induction period of 10–20 min, the pressure begins to drop as the reaction proceeds. Hydrogen is added to keep the pressure at 800 torr. The flow of hydrogen continues until enough has been added to satisfy the stoichiometry of the over-all reaction

$$2H_2 + CO_2 \longrightarrow C + 2H_2O$$

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(1) W. M. Rutherford and J. M. Keller, to be published.

(2) I. W. Ruderman and C. S. Wu, USAEC Report AECD-2412, 1948.

(3) P. L. Walter, J. F. Rakszawski, and G. R. Imperial, *J. Phys. Chem.*, 63, 133 (1959); 63, 140 (1959).

(4) The circulating pump is a miniature version of that described by J. F. Schultz, *Ind. Eng. Chem.*, **54**, 34 (1962).