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Eight-Coordinate Complexes of Cobalt(II). A Principle Influencing the Occurrence of High Coordination Numbers[1]

Sir:

Several years ago, compounds containing the tetra-nitratocobaltate(II) ion, $[Co(NO_3)_4]^{2-}$, were reported from several laboratories.[2,3] On the basis of its magnetic moment and its visible and infrared spectra, this complex ion was assigned a tetrahedral structure. However, as a result of subsequent investigations[4,5] of the compounds $Co(R_3MO)_2(NO_3)_2$, $R = CH_3$ or C_6H_5, $M = P$ or As, it was suggested that bidentate nitrate ions might also occur in $[Co(NO_3)_4]^{2-}$ with the over-all arrangement of oxygen atoms about the metal ion being such as to produce a ligand field of approximately tetrahedral symmetry, even though the actual disposition of oxygen atoms would not have this shape. We wish to report that a single crystal X-ray structure determination of $[As(C_6H_5)_4]_2[Co(NO_3)_4]$ demonstrates that this is indeed the case, each nitrate ion being bidentate, and the Co-(II) being eight-coordinate in a dodecahedral complex.

The complex was prepared by mixing stoichiometric quantities of $As(C_6H_5)_4Cl$, $AgNO_3$, and $CoCl_2$ in acetonitrile. After separating the insoluble AgCl by decantation, the solution was condensed to an oil by evaporation, and the remaining acetonitrile was extracted into ether. The complex was then recrystallized from a chloroform solution by addition of CCl_4. The unit cell is monoclinic, $a = 23.47$, $b = 11.34$, $c = 18.57$ Å., $\beta = 107°$, and contains two formula units. The space group is C2/c and the cobalt atoms occupy special positions requiring the $[Co(NO_3)_4]^{2-}$ ions to have C_2 symmetry axes. The eight oxygen atoms surrounding the cobalt atom lie at the vertices of a distorted dodecahedron. Figure 1 shows some of the important bond distances and interbond angles at the present stage of refinement, in which only isotropic temperature factors have been used. The complete structure can be obtained by rotating each of the nitrate ions shown about the C_2 axis.

Within the limits of error, the $[Co(NO_3)_4]^{2-}$ ion has only C_{2v}, rather than D_{2d} symmetry, but it is useful to divide the eight Co-O bonds into just two sets. In one, consisting of bonds from Co to O_I and O_{IV}, the Co-O distances are in the normal range for Co-O bonds, 2.02 and 2.05 Å.; in the other set of bonds, from Co to O_{II} and O_V, they are much longer, 2.41

(1) Research supported by a grant from the U. S. Army Research Office.
(2) F. A. Cotton and T. G. Dunne, *J. Am. Chem. Soc.*, **84**, 2013 (1962).
(3) D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, **1**, 848 (1962).
(4) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).
(5) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).
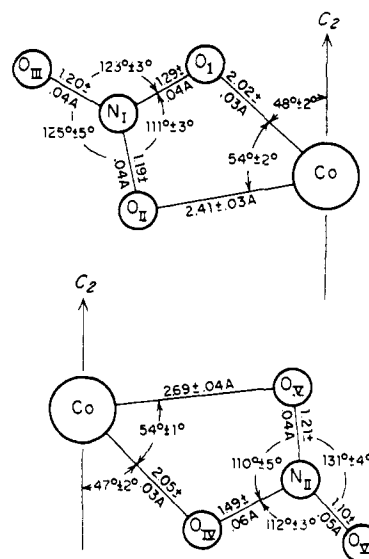

Figure 1.

and 2.69 Å., but still short enough to indicate a definite Co-O bonding interaction. The four short bonds approximately define an elongated tetrahedron with a vertical angle of 45–50°, while the four long ones define a severely flattened tetrahedron—very nearly a square—with a vertical angle of about 170°.

It has also been found that an analogous compound containing $(CF_3COO)^-$ in place of $(ONO_2)^-$ can be prepared, *viz.*, $[As(C_6H_5)_4]_2[Co(O_2CCF_3)_4]$. This has essentially the same spectrum and magnetic moment as the nitrato complex. It crystallizes in the tetragonal system, space group $I4_1/a$, $a = 11.68$ Å., and $c = 40.82$ Å., with four formula units per cell. It is thus required that the Co atoms lie at special positions with $\bar{4}$ symmetry and this makes it seem likely that the $[Co(O_2CCF_3)_4]^{2-}$ ion has an eight-coordinate structure similar to, but more regular than, that of $[Co(NO_3)_4]^{2-}$, although this is not absolutely required. A thorough investigation of the structure is in progress.

We believe that from the above results and other data in the literature, an interesting and useful structural principle may be inferred, namely, that a polyatomic ligand in which two *chemically equivalent* atoms are held much closer together than such a pair of atoms would be if independent of each other has a tendency to interact through both of the equivalent atoms in such a way that the mean positions of the pairs of atoms lie roughly at the vertices of one of the usual (*e.g.*, octahedral or tetrahedral) coordination polyhedra. This is a generalization of the earlier suggestion[5] that in the $Co(R_3PO)_2(NO_3)_2$ compounds, each nitrate ion as a whole occupies a vertex of a distorted tetrahedron about the cobalt ion.

In the $[Co(NO_3)_4]^{2-}$ ion, this tendency is manifested in the fact that all four of the nitrate ions present two oxygen atoms to the cobalt ion, and the centers of the nitrate ions (the N atoms) lie at the vertices of a flattened tetrahedron, the two N-Co-N angles bisected by the molecular C_2 axis being 152 and 144°. However, if lines are drawn to points along the $O\cdots O$ lines within nitrate ions, such that these points lie at distances from each oxygen atom which are inversely proportional to the distances of the oxygen atoms from the cobalt atom, angles between these lines are very

close to 109°. If the contribution of each oxygen atom to the ligand field is approximately proportional to the reciprocal of its distance from the metal ion, the metal ion should then experience a ligand field approximately tetrahedral in shape, in accord with the implications of the magnetic and spectroscopic results.

In $[Cr(O_2)_4]^{3-}$, where the short O–O distances are only 1.41 Å.[6] (as compared to ~2.1 Å. in NO_3^-), the structure is more regular, all Cr–O distances being within a range of 0.1 Å., and the centers of the four O_2^{2-} ions form a moderately flattened tetrahedron. In Co-$[(CH_3)_3PO]_2(NO_3)_2$, where there are only six oxygen atoms bonded to Co, both O atoms of each nitrate are about equidistant[4] from Co. Finally, in Mg_3Ce_2-$(NO_3)_{12} \cdot 24H_2O$, each cerous ion is surrounded by six nitrate ions, each presenting two of its oxygen atoms to the cation. The actual coordination number is 12 and the coordination polyhedron is a distorted icosahedron, but the midpoints of the pairs of coordinated oxygen atoms lie approximately at the vertices of an octahedron.[7]

(6) J. D. Swalen and J. A. Ibers, J. Chem. Phys., **37**, 17 (1962).

(7) A. Zalkin, J. D. Forrester, and D. H. Templeton, ibid., **39**, 2881 (1963).

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The 3,2,1-Bicyclic Reaction Path

Sir:

Three-, four-, five-, and six-centered reaction paths have been used to describe the course of many reactions in organic chemistry. Herein is described a 3,2,1-bicyclic path which may prove to be of general importance because in three instances of competition the 3,2,1-bicyclic path wins out over four- and six-centered paths.

When *o*-benzoylbenzoic acid (I) is treated with thionyl chloride, the cyclic acid chloride II is produced.[1] We picture this reaction as proceeding through the 3,2,1-bicyclic path as shown below.
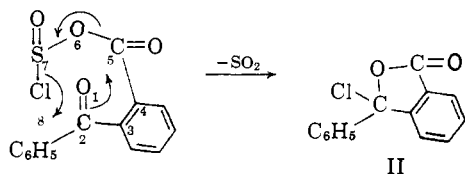
Carbon atoms 2 and 5 are the bridgehead atoms in this example and the three connecting links in the 3,2,1-bicyclic transition state are, respectively, the carbonyl oxygen (1), the aromatic carbons (3 and 4), and the oxygen–sulfur–chlorine grouping (6, 7, and 8). In competition with the formation of II is the usual four-centered path involved in forming acid chlorides from acids such as benzoic. The latter path wins out when *o*-mesitoylbenzoic acid is treated with thionyl chloride as infrared analysis shows that the normal acid chloride is formed.

(1) McRenson, Bull. soc. chim. Belges, **70**, 77 (1961) shows that o-phthalaldehydic, o-acetylbenzoic, and o-benzoylbenzoic acid chlorides exist mainly, if not entirely, in the cyclic structure, but no mechanism to account for their formation has been proposed.

Another case, wherein the competition lies between a six-atom cyclic mechanism and the 3,2,1-bicyclic path, is that of the treatment of *o*-benzoylbenzoic acid with ethoxyacetylene. The normal–pseudo anhydride IV is produced from the postulated intermediate III which would be expected to yield the normal–normal anhydride V if the six-atom mechanism[2] obtained.
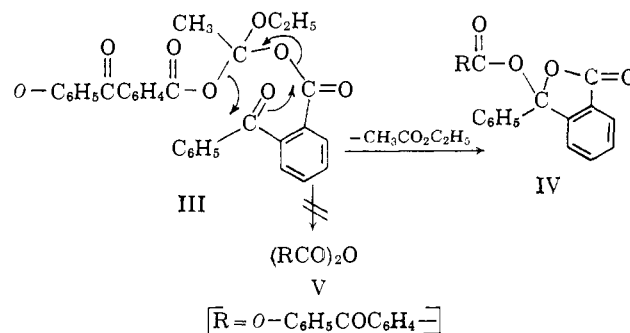
We have shown that the anhydride, m.p. 140°, produced has structure IV contrary to other conclusions.[3] The absorption spectrum of an equimolar mixture of normal and pseudo methyl *o*-benzoylbenzoates proved to be almost identical through the range 260–340 mμ to that of 1 equiv. of the anhydride (IV).

The third example of the involvement of the 3,2,1-bicyclic path is supplied by the fact that when sodium *o*-benzoylbenzoate is treated with methyl chlorosulfite, an intermediate VI is formed which decomposes to yield the pseudo methyl ester VII[4] almost exclusively, as shown below.
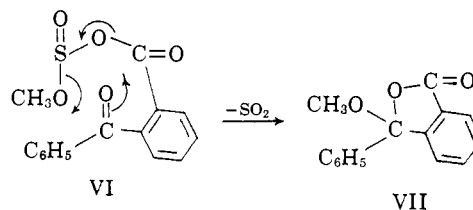
This example provides convincing evidence for the 3,2,1-bicyclic path since the normal methyl ester of *o*-benzoylbenzoic acid is the stable isomer. As far as the mechanism of formation of ester from a simple acid by this procedure is concerned, either a four- or six-atom cyclic path can be pictured, depending on whether oxygen A or B of intermediate $\underset{A}{R}COO\underset{B}{S}OR'$ is retained in the ester formed.[4]

In the three cases cited as evidence for a 3,2,1-bicyclic path, the reactions involve compounds which have two carbonyl groups in the 1,4-position. Since α-acylamino and α-acetoxy acids each have this feature, further exploration of the generality of this path seems desirable. It has already been claimed that a 3,2,1-bicyclic compound is involved in the "amino-

(2) H. H. Wasserman and P. S. Wharton, J. Am. Chem. Soc., **82**, 3457 (1960), and references therein.

(3) H. Schmid, M. Hochweber, and H. V. Halben, Helv. Chim. Acta., **31**, 354 (1948), reported that since the ultraviolet absorption spectra of the anhydride and normal methyl o-benzoylbenzoate were fairly close in the 260–290 mμ region, the anhydride had normal–normal structure, V. If the anhydride really had structure V the intensity of this absorption should have been about double.

(4) M. S. Newman and W. S. Fones, J. Am. Chem. Soc., **69**, 1046 (1947), have shown that sodium salts of a variety of acids are converted into intermediates, $RCO_2SO_2C_4H_{9-n}$, by treatment with n-butyl chlorosulfite. On warming, these intermediates evolve sulfur dioxide and yield butyl esters.