Inorganica Chimica Acta, 20 (1976) L27 - L28

A Pentagonal Bipyramidal Scandium(III) Complex: Synthesis and Characterization of Diaqua(2,6-diacetylpyridine bis-semicarbazone)scandium(III) Hydroxide Dinitrate

D. D. McRITCHIE, R. C. PALENIK and G. J. PALENIK

Center for Molecular Structure, Department of Chemistry, University of Florida, Gainesville, Florida 32611, U.S.A.

(Received August 18, 1976)

Seven coordination is rare for all elements but particularly for the smaller elements of the fourth row [1]. With the exception of scandium for which no seven coordinate complexes have been reported, there are one or two examples of seven coordination known for each of the elements from Ca through Zn. The absence of seven-coordinate Sc complexes was surprising since crystal field effects should not be important in the Sc(III) ion. Consequently, we decided to study the reaction of Sc(III) salts with the planar pentadentate ligand 2,6-diacetylpyridinebissemicarbazone, dapsc [2], and have now prepared and characterized in the first pentagonal bipyramidal complex of Sc(III), diaqua(2,6-diacetylpyridinebissemicarbazone)scandium(III) hydroxide dinitrate, I.

Hydrated scandium nitrate (obtained from the oxide and nitric acid) was combined on a 1:1 mol basis with dapsc in 50 ml of 1:1 ethanol–water. The bright yellow suspension was heated to about 55 °C and stirred for 1 hour, the solid gradually disappearing. After filtering and cooling, a bright yellow solid precipitated. Slow evaporation of the filtrate gave crystals of I suitable for X-ray diffraction studies. The infrared spectrum of I in nujol showed sharp absorption bands at 1700, 1645, 1600, and 1550 cm^{-1}. Although I does not melt below 300 °C, the yellow solid turns orange at 180 °C and bright red by 184 °C.

Crystal Data

$C_{11}H_{20}N_9O_{11}Sc$, $[Sc(dapsc)(OH_2)_2]^{+3}(NO_3^-)_2(OH^-)$: $M = 499.29$, monoclinic, $P2_1/n$, $a = 11.818(9)$, $b = 14.785(9)$, $c = 12.046(6)$ Å, $\beta = 105.37(5)°$, $D_m = 1.63$ g cm^{-3}, $Z = 4$, $D_c = 1.634$ g cm^{-3}. The intensity data were measured using a Syntex P$\bar{1}$ diffractometer with a variable speed (1 to 24°/min) scan technique and nickel filtered Cu-K$_\alpha$ radiation. The structure was solved by the heavy atom method and refined by least-squares techniques to a final R value ($R = \Sigma \Delta F/\Sigma F_{obs}$) of 0.053 for the 2028 reflections used in the analysis.

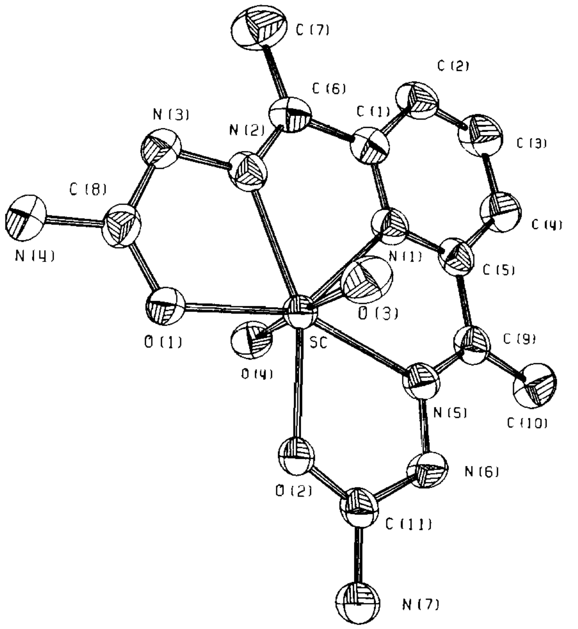

Figure 1. An ORTEP drawing of the diaqua(2-6-diacetylpyridinebissemicarbazone)scandium(III) cation, showing the pentagonal bipyramidal geometry, thermal ellipsoids and atomic numbering. Pertinent distances and angles are: Sc–N(1), 2.285; Sc–N(2), 2.258(4); Sc–N(5), 2.305(4); Sc–O(1), 2.098(3); Sc–O(2), 2.137(3); Sc–O(3), 2.084(4); and Sc–O(4), 2.123(4) Å; N(1)–Sc–N(5), 67.0(1); N(5)–Sc–O(2), 69.1(1); O(2)–Sc–O(1), 84.7(1); O(1)–Sc–N(2), 70.4(1); and N(2)–Sc–N(1), 68.9(1)°.

Figure 1 clearly shows the PBP nature of the cation. The scandium atom and the ligand dapsc, excluding C(10), are remarkably planar. The average deviation is only 0.023 Å [with a maximum deviation of 0.070 Å for O(1)] for the 20 atoms used to define the plane. The methyl group C(10) is 0.184 Å from the plane. The deviations from planarity in the scandium complex are smaller than those observed in other PBP complexes with the dapsc ligand. Presumably, the spherical electron distribution and size of the Sc(III) ion account for the planarity of the cation.

The Sc–N distances average 2.283 Å and the Sc–O distances average 2.110 Å. However, there are small but significant differences between chemically equivalent scandium–donor atom distances, *i.e.* the Sc–O differs by 0.039 Å and Sc–N by 0.049 Å. The reasons for these differences may involve either hydrogen bonding or non-bonded contacts. Although no seven-coordinate scandium structures are available for a comparison, the Sc–O distances are in the middle of the range (2.017 to 2.183 Å) reported for octahedral complexes [3] and slightly smaller than the range of Sc–O distances (2.161 to 2.314 Å) found in the eight-coordinate tetrakis(tropolonato)-scandium(III) [4, 5].

In conclusion, we see that PBP complexes of a variety of elements can be prepared using suitably designed ligands. However, the subtle factors involving the distances and angles in PBP complexes are not completely understood and await additional studies.

Acknowledgment

We thank the Center for Instructional and Research Computing Activities, University of Florida, for a grant of computer time and the National Science Foundation for partial financial support.

References

1 See for example recent inorganic texts such as (a) J. J. Lagowski, 'Modern Inorganic Chemistry', Marcel Dekker, New York, 1973, p. 629; (b) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Interscience, New York, 1972, 3rd ed., p. 1070; (c) J. E. Huheey, 'Inorganic Chemistry', Harper and Row, New York, 1972, p. 401; (d) W. L. Jolly, 'The Principles of Inorganic Chemistry', McGraw-Hill, New York, 1976, p. 247.

2 G. J. Palenik, D. W. Wester, U. Rychlewska and R. C. Palenik, *Inorg. Chem.*, in press, and references therein.

3 M. E. Hursthouse in 'Molecular Structure by Diffraction Methods', Vol. 3, p. 407, 1975.

4 A. R. Davis and F. W. B. Einstein, *Inorg. Chem., 13,* 1880 (1974)

5 T. J. Anderson, M. A. Newman and G. A. Melson, *ibid.*, 1884.