A Tetranuclear Oxopivalate of Cobalt(II)

By A. B. BLAKE

(*Department of Chemistry, University of Hull*)

THE compound of formula $Co_4O(OCO{\cdot}CMe_3)_6$ has been prepared by the vacuum pyrolysis of anhydrous cobalt pivalate at 220—230°. The product sublimes as deep blue octahedral crystals, up to 2 mm. long, and is soluble in dry benzene or carbon tetrachloride without decomposition. The method of preparation, analysis, and molecular weight support the above formula, and indicate a structure analogous to that of the well-known beryllium and zinc oxoacetates,[1] consisting of a central oxygen atom surrounded tetrahedrally by four metal atoms, the latter being connected in pairs by bidentate carboxyl groups. The crystalline unit cell is cubic, space group *Pa*3, with $a = 20{\cdot}33 \pm 0{\cdot}05$Å, and contains eight molecules (density calculated, $1{\cdot}36 \pm 0{\cdot}01$; found, $1{\cdot}36 \pm 0{\cdot}02$). The molecular symmetry is therefore C_3, the highest symmetry possible with the assumed structure.

The spectrum of a carbon tetrachloride solution has maxima at 7210 ($\epsilon = 310$), 8460 ($\epsilon = 280$), 16,200 (sh, $\epsilon = 2660$), 17,000 ($\epsilon = 2740$), and 18,320 cm.$^{-1}$ ($\epsilon = 1330$), and is quite similar to the spectrum of cobalt(II) in concentrated alkali solutions,[2] which contain the tetrahedral anion $[Co(OH)_4]^{2-}$ or $[Co(OH)_3H_2O]^-$. Assuming an approximately tetrahedral ligand field, and using the values $\nu_2 = 7800$, $\nu_3 = 17{,}000$ cm.$^{-1}$, we calculate[3] the spectroscopic parameters $\Delta = 4540$, $B = 745$ cm.$^{-1}$.

The compound is of particular interest magnetically, since it provides an opportunity to study the exchange interaction in an isolated cluster of four magnetic ions. That such interaction occurs is indicated by the abnormally low effective magnetic moment of $3{\cdot}86 \pm 0{\cdot}05$ B.M. per cobalt atom at room temperature (measured susceptibility at 296° K, $26{,}200 \pm 300$; calculated diamagnetic susceptibility, -435; calculated temperature-independent paramagnetic susceptibility,[2] 1760, all in e.m.u. per mole $\times 10^6$). This may be compared with moments of 4·4—4·8 B.M. usually observed[2] for magnetically dilute tetrahedral cobalt(II) compounds, or with the predicted moment of $4{\cdot}38 \pm 0{\cdot}05$ B.M. calculated from the above value of Δ, assuming[2] a value of -147 ± 10 cm.$^{-1}$ for the spin–orbit coupling constant λ. An investigation of the temperature-dependence of the susceptibility is now in hand.

(*Received, July 20th*, 1966; *Com.* 522.)

---

[1] G. T. Morgan and W. T. Astbury, *Proc. Roy. Soc.*, 1926, *A*, **112**, 441; H. Koyama and Y. Saito, *Bull. Chem. Soc. Japan*, 1954, **27**, 112.

[2] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.

[3] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, 1954, **9**, 753; F. A. Cotton and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 1777.