A New Cluster Carbonylcobaltate

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CLUSTER carbonylmetallates are known for a number of transition metals, but in the first row cobalt is apparently an exception as it gives only the well known derivatives of $Co(CO)_4^-$. The reported cluster carbonylmetallate $FeCo_3(CO)_{12}^-$ contains iron as well as cobalt.[1] We now report the preparation of derivatives of the pentadecacarbonylhexacobaltate(—II), $Co_6(CO)_{15}^{2-}$.

When a red concentrated solution of $[Co(EtOH)_x][Co(CO)_4]_2$ obtained from $Co_2(CO)_8$ and ethanol,[2] was boiled *in vacuo* at 60° for 8 hr., the colour changed to deep green and on evaporation of the ethanol a mixture of $[Co(EtOH)_x]$-$[Co_8(CO)_{15}]$ and minor amounts of $[Co(EtOH)_x]$-$[Co(CO)_4]_2$ and $Co_4(CO)_{12}$ was left. Water extraction of this reaction product gave a green–yellow solution containing the two ionic species which were separated by addition of solid potassium bromide. The crystalline $K_2Co_6(CO)_{15}$ was precipitated in yields that, in the best preparative conditions, account for about 80% of the starting $Co_2(CO)_8$. From water solutions of $K_2Co_6(CO)_{15}$ the cæsium, the tetramethyl, and the tetraethylammonium salts were easily obtained, in an analytically pure state, by double exchange reactions.

These salts are dark green diamagnetic solids, soluble in acetone, tetrahydrofuran, and methanol; the solutions are very sensitive to air oxidation and react with carbon monoxide at normal pressure and room temperature. This reaction was studied in pyridine where the tetraethylammonium salt reacts with carbon monoxide giving a mixture of $NEt_4Co(CO)_4$ and $[Co(C_5H_5N)_6]$ $[Co(CO)_4]_2$.

In tetrahydrofuran solution the i.r. spectra show three bands assigned to terminal carbonyl groups at about 2040 (m), 1980 (s), and 1960 (shoulder) cm.$^{-1}$ and three bands assigned to bridging carbonyl groups at about 1780 (s), 1735 (s), and 1680 (w) cm.$^{-1}$.

We have not been able to isolate the corresponding hydridocarbonyl $H_2Co_6(CO)_{15}$; by addition of an excess of hydrogen chloride at —70° to a solution of the potassium salt in tetrahydrofuran we could only obtain the unstable derivative $KHCo_6(CO)_{15}$.

The structure of the pentadecacarbonylhexacobaltate (—II) anion can be tentatively derived from that of $Rh_6(CO)_{16}$, by removal of one of the four bridging groups.[3] A detailed *X*-ray-structural study is now under way.

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