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Oxidative Decarbonylation of Dicobalt Octacarbonyl by Pyridine Carboxylic Acids

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The oxidative decarbonylation of the group VI hexacarbonyls ($Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$) by pyridine-2-carboxylic acid (picolinic acid), abbreviated picH, provides a convenient route to the six and eight-coordinate complexes of the types $M(pic)_3$, where M = Cr or Mo [2], and $M(pic)_4$, where M = Mo or W [2–4]. In the case of the reaction between $Re_2(CO)_{10}$ and molten picolinic acid [5], oxidation does not proceed beyond the Re(I) state, and the presence of pyridine in the resultant product, $Re(CO)_3(py)(pic)$, attests to the thermal decarboxylation of a portion of the picolinic acid. We now communicate some results concerning the reactions of dicobalt octacarbonyl with picolinic acid and dipicolinic acid (pyridine-2,6-dicarboxylic acid), abbreviated $dipicH_2$, which reveal several features of note.

The reaction between $Co_2(CO)_8$ and an excess of dipicolinic acid (1:8 mol proportions) in refluxing methanol produces the insoluble polymeric complex $[Co(dipic)]_n$ in very high yield. This bright purple complex has identical spectroscopic properties to those exhibited by samples of this complex prepared by the reaction of the tetrameric acetylacetonate complex $[Co(acac)_2]_4$ with dipicolinic acid in refluxing ethanol [6]. Although an oxidative decarbonylation also occurs upon reacting $Co_2(CO)_8$ with picolinic acid (under these same reaction conditions), the nature of the reaction product is quite different since carbonyl groups are still present (intense ν_{CO} absorptions at 1900 and 1875 cm^{-1}).** The microanalytical data for this product (Found: C, 44.57; H, 3.54; N, 7.79%) did not appear to conform to any obvious stoichiometry until we discovered that most of the features in the IR spectrum** of this complex showed a striking resemblance to the related spectrum of the complex $[Co_2(picH)_3(pic)_3]HSO_4\cdot 1/2H_2O$,† which we had prepared in an earlier study [7]. It then became apparent that the product of the reaction of $Co_2(CO)_8$ with picolinic acid is the salt $[Co_2(picH)_3(pic)_3]Co(CO)_4\cdot 3H_2O$ (Calcd.: C, 44.54; H, 3.08; N, 7.79%). While the ν_{CO} mode of the $Co(CO)_4^-$ anion is split (by ~ 25 cm^{-1}) due to low site symmetry effects, its position (at ~ 1900 cm^{-1}) is characteristic of this species [8]. Further characterization studies on this complex revealed the following features. (1) Its electronic absorption spectrum (solid-state) is essentially the same as that of $[Co_2(picH)_3(pic)_3]HSO_4\cdot 1/2H_2O$, with prominent absorptions at 1080, 530sh and 490 nm. (2) The magnetic moment (μ_{eff}) of $[Co_2(picH)_3(pic)_3]Co(CO)_4\cdot 3H_2O$, 4.08 BM/Co, is in agreement with that calculated assuming a paramagnetic $[Co_2(picH)_3(pic)_3]^+$ cation, with a magnetic moment of 5.00 ± 0.05 BM/Co atom,‡ and a diamagnetic $Co(CO)_4^-$ anion. (3) In spite of the two distinct cobalt species which are within this molecule, the measurement of the Co $2p_{1/2,3/2}$ X-ray photoelectron spectrum of this complex [9] did not reveal two sets of binding energy peaks. Clearly, the Co $2p_{1/2,3/2}$ energies of the $[Co_2(picH)_3(pic)_3]^+$ and $Co(CO)_4^-$ ions are fortuitously coincident (at least within the current limits of resolution of our XPS spectrometer).

While the ligand induced disproportionation of $Co_2(CO)_8$ to produce complexes of the type $[CoL_6]^{2+}[Co(CO)_4^-]_2$ is well documented [10], the formation of the $[Co_2(picH)_3(pic)_3]^+$ cation by such a reaction is most unusual since it is only the second report of the formation of dimeric metal picolinate complexes of this type. These and related oxidative decarbonylation reactions are currently being further investigated.

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**IR spectra were recorded on Nujol mulls due to the insolubility of this complex in suitable organic solvents.

†This complex, in turn, has an IR spectrum which is the same as other derivatives of the type $[M_2(picH)_3(pic)_3]X\cdot nH_2O$, where M = Ni or Fe and X = Cl, NO_3, HSO_4, PF_6 or $1/2(S_2O_8)$ with the exception of bands due to the different anions (see ref. 7).

‡This is the experimentally determined magnetic moment for the complex $[Co_2(picH)_3(pic)_3)HSO_4\cdot 1/2H_2O$.