Synthesis and Characterization of Tetranitrosylchromium

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Summary Photolysis of $Cr(CO)_6$ in pentane solution with an excess of NO results in the formation of $Cr(NO)_4$ which has been characterized by Raman and i.r. studies.

THREE four-co-ordinate transition metal nitrosyl complexes which are isoelectronic with $Ni(CO)_4$ are known: $(NO)_3Mn(CO)$, $(NO)_2Fe(CO)_2$, and $(NO)Co(CO)_3$. The last and most elusive member of this series, $(NO)_4Cr$, has now been prepared by photolysis of a pentane solution of $Cr(CO)_6$ in the presence of NO. The formula $(NO)_4Cr$ was verified by the mass spectrum which shows m/e numbers corresponding to the parent ion, Cr, and NO. The i.r. spectrum of $(NO)_4Cr$ in pentane showed a single N–O stretching mode at 1716 cm^{-1}. While no band was observed in the NO bridging region (*ca.* 1400 cm^{-1}) this region is partially obscured by pentane vibrations. The absence of bridging NO groups was verified by a Raman spectrum of solid $(NO)_4Cr$ at *ca.* 78 K. Only two N–O stretching modes were observed at 1694 and 1777 cm^{-1} in the Raman effect. The Raman and i.r. data indicate T_d molecular symmetry. The consistency of solution and solid state vibrational data suggest that T_d symmetry is maintained in the solid state.

For the preparation of $(NO)_4Cr$ best results were obtained by photolysing *ca.* 500 mg of $Cr(CO)_6$ in 150 ml of outgassed pentane.† Nitric oxide was bubbled through the pentane solution before and during photolysis. A 450 watt Hg lamp in a quartz immersion cell with a Corex filter was used. The solution begins to turn red within 10 min indicating the formation of $(NO)_4Cr$. The reaction was monitored by i.r. and was complete after about 1 h of photolysis. The red solution was then separated by filtration from an orange solid, which also formed during photolysis. The $(NO)_4Cr$ was separated from pentane by trap to trap vacuum distillation. The red pentane solution of $(NO)_4Cr$ was stable when stored under an atmosphere of NO.

$(NO)_4Cr$ is a red-black solid at room temperature and is completely soluble in non-polar solvents. Its solubility in stopcock grease and high air sensitivity required that all manipulations be carried out on a grease free vacuum system. $(NO)_4Cr$ behaves much like $(NO)_3Mn(CO)$ and can be transferred (with some difficulty) under vacuum. Unfortunately, gaseous $(NO)_4Cr$ decomposes slowly under a vacuum to give NO and lustrous metallic chromium. The complex can be stored at −20° in an evacuated vessel without decomposition.

The intensity of the Raman band at 1777 cm^{-1} is *ca.* 1/4 that of the 1694 cm^{-1} F_2 mode. Whilst it is odd that the totally symmetric N–O stretch is less intense in the Raman effect than the asymmetric stretch the same behaviour was noted for $Ni(CO)_4$.[1]

The N–O stretching frequencies for $(NO)_4Cr$ are slightly lower than those of $(NO)_3Mn(CO)$[2] following the monotonic decrease noted in going from $(NO)Co(CO)_3$ to $(NO)_2Fe(CO)_2$ to $(NO)_3Mn(CO)$. While this decrease suggests a lower N–O bond order in going from $(NO)Co(CO)_3$ through $(NO)_4Cr$ definitive evidence must await detailed vibrational analysis.

This is the second example of a binary metal nitrosyl; the first being $(NO)_3Co$.[3] Of particular interest will be comparisons of bond lengths and potential constants for $(NO)_4Cr$

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† Chromatographic grade pentane must be used.

with those of the isoelectronic and isostructural $Ni(CO)_4$.[4] $(NO)_4Cr$ is particularly amenable to detailed vibrational analysis as many isotopically substituted species can be obtained.

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