

Metal Carbonyl Thionitrosyl Complexes

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Summary The polymeric thionitrosyl metals formulated previously as $M(N_4S_4)$ ($M = Fe$ or Co), have been reinvestigated and new iron and cobalt carbonyl thionitrosyl complexes, $Fe(CO)N_4S_4$ and $Co_2(CO)N_4S_4$ containing some of the highest $\nu(C-O)$ frequencies observed in transition metal carbonyls have been prepared.

THE complexes formed between tetrasulphur tetranitride and transition metals were initially formulated as thionitrosyl metals, $M(N_4S_4)$ ($M = Fe, Co, Pd, Pt$ or Ni),¹ and later² reformulated as $M(HN_2S_2)_2$. The nature of these insoluble, presumably polymeric, products of the above type is still unclear.³

We have reinvestigated the reaction of pentacarbonyliron and N_4S_4 by dissolving the latter in dry, deoxygenated benzene, adding various molar ratios (1:1, 1:2, 2:1) of $Fe(CO)_5$ directly and maintaining the reaction at 60–70 °C for ca. 6 h. In all cases, a black insoluble compound, $Fe(CO)N_4S_4$, was obtained; 4 mol. of CO per mol. of $Fe(CO)_5$ which had reacted were evolved. The compound decomposes on exposure to air and is shock-sensitive; it should not be handled dry in greater than 100 mg amounts.† The mass spectrum gave no parent-ion peak but CO was evolved preferentially at ca. 90 °C followed at higher temperatures by N_2 and other thermal fragmentation products of N_4S_4 (e.g. S_8^+). Similarly, $Co_2(CO)(N_4S_4)$ was obtained as an insoluble, explosive black solid by the reaction of octacarbonyldicobalt and N_4S_4 in benzene at room temperature;† the mass spectrum confirmed the presence of CO. The

cobalt compound, unlike the iron complex, reacts with refluxing ether or acetone to give the known soluble monomeric $Co(HN_2S_2)_2$.² The i.r. spectra of the above polymeric complexes (measured for both mulls and discs) gave no absorption in the $\nu(N-H)$ region but gave relatively intense $\nu(C-O)$ bands at ca. 2180 cm^{-1} . In contrast the soluble cobalt compound, $Co(HN_2S_2)_2$, gave definite bands at 3260 and 3120 cm^{-1} but no absorption in the 2200–1900 cm^{-1} region.

We formulate these complexes as polymeric thionitrosyl-carbonyl metals, $Fe(CO)N_4S_4$ and $Co_2(CO)N_4S_4$. The $\nu(C-O)$ values are very high for formally zero-valent complexes and indicate weak M–C bonds consistent with the preferential loss of CO. A comparable $\nu(C-O)$ value has been reported for $Mo(CO)N_5S_5$.⁴ The absence of any well defined $\nu(M-S)$ i.r. frequencies suggests bonding of the N_4S_4 ligand *via* the nitrogen atoms and if each N_4S_4 bonds to two metal atoms, a polymeric structure may be obtained. The high $\nu(C-O)$ frequency is probably related to the powerful electron-attracting nature of the N_4S_4 ligand possibly with some direct interaction of the positive sulphur atoms⁵ with the metal orbitals. We have obtained similar products by the reaction of N_4S_4 with a number of iron carbonyl complexes and further work is in progress.

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† Satisfactory elemental analyses were obtained for all elements including oxygen.

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