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Preliminary communication

Preparation and characterisation of $[Re(CO)_2NO(NO_3)_2]_2$

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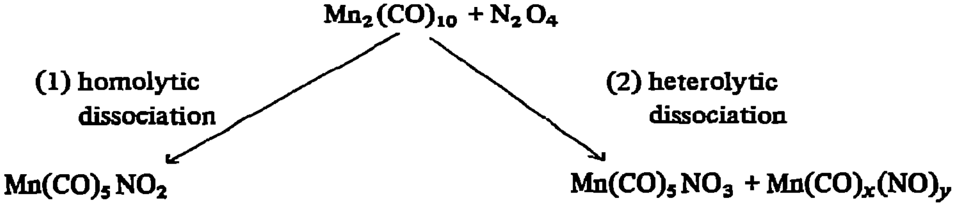
SUMMARY

The binuclear compound $[Re(CO)_2NO(NO_3)_2]_2$ (I) has been isolated as a minor product of the reaction of $Re_2(CO)_{10}$ and N_2O_4; spectral evidence indicates the metal atoms in I are linked by two bridging nitrate groups.

The reaction of dimanganese decacarbonyl with dinitrogen tetroxide yields nitro-, nitrito- and nitrato-pentacarbonylmanganese (I) together with an uncharacterised manganese carbonyl nitrosyl, $Mn(CO)_x(NO)_y$[1]. On the basis of these observations the authors suggested that this reaction may proceed via two routes involving both homolytic and heterolytic dissociation of N_2O_4, *viz.*:



Previous examination of the analogous reaction of dirhenium decacarbonyl led to the isolation of only $Re(CO)_5NO_3$, although the presence of the corresponding nitro- and nitrito-species was inferred from the infrared spectrum of the crude reaction product. On this basis a homolytic dissociation mechanism, analogous to route (1) above, was inferred, the nitrato species being formed by subsequent oxidation of $Re(CO)_5ONO$ with excess N_2O_4[2].

The reaction of $Re_2(CO)_{10}$ and N_2O_4 has now been re-examined and a small yield of a nitrosyl containing product isolated and characterised.

Dirhenium decacarbonyl was allowed to react with liquid dinitrogen tetroxide at 0° under an inert atmosphere, over a period of 3 hours. Excess dinitrogen tetroxide was removed by warming the mixture to 35–40° and the resulting buff coloured solid dissolved in dry methanol. Fractional crystallisation of this solution yielded pure $Re(CO)_5NO_3$ [2] in the early fractions, the latter fractions containing a mixture of $Re(CO)_5NO_3$ and compound (I) giving rise to infrared absorptions at 2161 w, 2110 s, 2060 s, 2047 s, 1996 m and 1800 s cm^{-1} ($CHCl_3$ solution). Two more fractional crystallisations of this mixture from methanol gave small yellow crystals of (I) in a pure state. Elemental analysis for rhenium, carbon and nitrogen indicated the empirical formula $ReC_2N_3O_8$. (Yield; 5% based on $Re_2(CO)_{10}$). The infrared spectrum of (I) showed bands at 2110 s, 2060 s and 1800 s ($CHCl_3$ solution), very similar to those observed for the complexes $[Re(CO)_2(NO)X_2]_2$ (X = Cl, Br, I)[3] and bands at 1520 s, 1495 s, 1296 sh, 1280 s, 1000 m, 993 m and 802 w cm^{-1} (Nujol mull), characteristic of coordinated nitrate groups[4]. Examination of the mass spectrum of (I) showed the ion of highest *m/e* to be 790 which indicates the dimeric formulation of (I) as $Re_2(CO)_4(NO)_2(NO_3)_4$ (based on ^{185}Re). Fragment ions characteristic of this formulation for (I) are also observed and it is of interest that although $Re_2(NO_3)_2^+$ and $Re_2(NO_3)^+$ are observed, no ion was found corresponding to Re_2^+. On the basis of this observation one may possibly infer that (I) contains metal atoms bridged by two nitrate groups rather than by a direct metal—metal bond.

Although an unequivocal assignment of the mode of coordination of the nitrate groups cannot be made on the basis of infrared data alone[4], the bands at 1495, 1280 and 993 cm^{-1} are very similar both in position and intensity to those observed for $Re(CO)_5NO_3$ [2], which has been shown by X-ray structural studies[5] to contain an unidentate nitrate group. The remaining N—O stretching frequencies at 1520, 1296 and 1000 cm^{-1} are very similar to those reported for compounds containing bridging nitrate groups[4].

Thus, the vibrational and mass spectral data is consistent with (I) adopting either of the two structures shown in Fig. 1. These structures, both of which are predicted to show the same spectral features, are closely related to that proposed for the analogous halogeno complexes[3]. It therefore appears that the mechanism of the reaction between

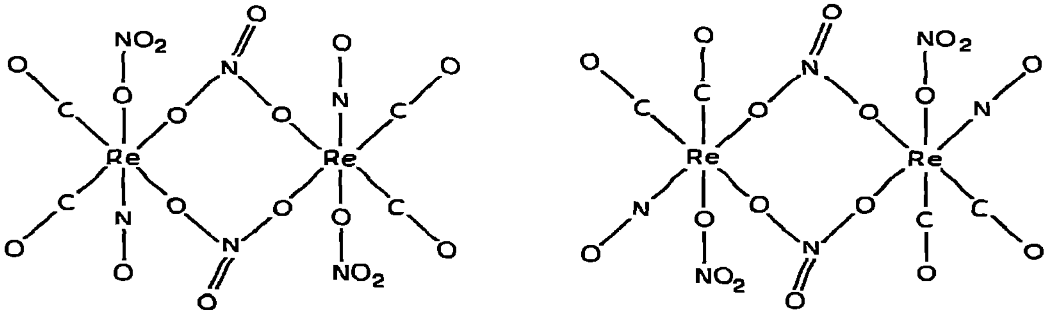


Fig. 1. Possible structures for I.

$Re_2(CO)_{10}$ and N_2O_4 more closely parallels that of $Mn_2(CO)_{10}$ than had previously been thought. Addison *et al.*[6] have recently reported the formation of the $N_4O_6^{2+}$ cation in the reaction of $Fe(NO_3)_3$ with N_2O_4 and further work is in progress in order to ascertain whether this species is involved in the reactions discussed above.

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