

Preparation and Crystal Structure of Tris- μ -azido-hexacarbonyldimanganate(I) Anion, $[(\text{CO})_3\text{Mn}(\text{N}_3)_3\text{Mn}(\text{CO})_3]^-$, and of Related Complexes

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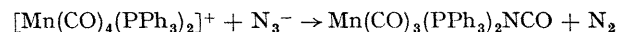
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Summary The synthesis and crystallographic characterisation of the tris- μ -azido-hexacarbonyldimanganate(I) anion are reported together with related azido- and isocyanato-complexes of manganese and rhenium.

THE metal hexacarbonyls of Group VIA elements¹ and cationic carbonyl metal complexes² react with the azide ion to give isocyanato-complexes. We report here the reactions of pentacarbonyl-manganese and -rhenium halides with N_3^- . These reactions proved to be rather complex since both azide and isocyanate ligands may be present in

$[\text{Re}_2(\text{CO})_6\text{X}_4]^{2-}$ (X = Cl, Br) have been recently reported.³ The dimeric azido-isocyanato-manganate and -rhenate react with triphenylphosphine, splitting of the azide bridges giving mixtures of $\text{M}(\text{CO})_3(\text{PPh}_3)_2\text{N}_3$ and $\text{M}(\text{CO})_3(\text{PPh}_3)_2\text{NCO}$ (M = Mn, Re). Monomeric bis(triphenylphosphine)manganese carbonyl complexes $\text{Mn}(\text{CO})_3(\text{PPh}_3)_2\text{X}$ (X = N_3 , NCO) have been obtained also from $\text{Mn}(\text{CO})_5\text{Cl}$ and NaN_3 or KOCN , respectively, and from $[\text{Mn}(\text{CO})_4(\text{PPh}_3)_2]\text{AlCl}_4$ and NaN_3 in ethanol (20°) according to the scheme,

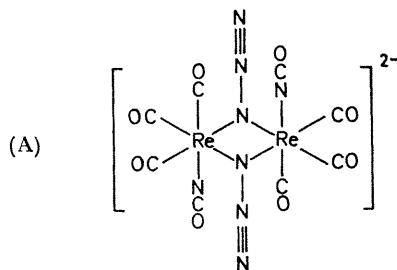


$\nu(\text{CO})$ and $\nu_{\text{as}}(\text{N}_3)$ bands of azido- and isocyanato-carbonyl-manganese and -rhenium complexes

	$\nu_{\text{as}}(\text{N}_3)$	$\nu_{\text{as}}(\text{NCO})$	$\nu(\text{CO})$
$\text{NEt}_4[\text{Mn}_2(\text{CO})_6(\text{N}_3)_3]^{\text{a}}$	2070s		2022s(A_2''), 1928vs(E')
$\text{NEt}_4[\text{Mn}_2(\text{CO})_6(\text{N}_3)_x(\text{NCO})_{3-x}]^{\text{a}}$	2079s	2190m	2025s, 1932vs
$[\text{Ph}_3\text{PNPPh}_3][\text{Mn}_2(\text{CO})_6(\text{NCO})_3]^{\text{b}}$		2183vs	2030m, 1935vs
$\text{Mn}(\text{CO})_3(\text{PPh}_3)_2\text{N}_3^{\text{c}}$	2058w		2029w, 1948s, 1911m
$\text{Mn}(\text{CO})_3(\text{PPh}_3)_2\text{NCO}^{\text{b}}$		2238s	2043w, 1955vs, 1925m
$\text{NEt}_4[\text{Re}_2(\text{CO})_6(\text{N}_3)_2(\text{NCO})_2]^{\text{a}}$	2088s	2223s	2007s, 1880vs
$\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{N}_3/\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{NCO}^{\text{b}}$	2059s	2238m	2026s, 1944s, 1903s, 1838m

^a In acetone; ^b in CHCl_3 ; ^c in benzene.

the reaction products, depending on the reaction conditions. The reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with a large excess of NaN_3 in water-ethanol at 20° gives the yellow diamagnetic dimeric anion $[\text{Mn}_2(\text{CO})_6(\text{N}_3)_3]^{2-}$.³ The position, number and intensity of the observed $\nu(\text{CO})$ and $\nu_{\text{as}}(\text{N}_3)$ stretching bands of $\text{NEt}_4[\text{Mn}_2(\text{CO})_6(\text{N}_3)_3]$ are consistent with a structure of D_{3h} symmetry and bridging azide groups (see Table). Reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with NaN_3 , LiN_3 , or NEt_4N_3 in tetrahydrofuran at higher temperatures yields

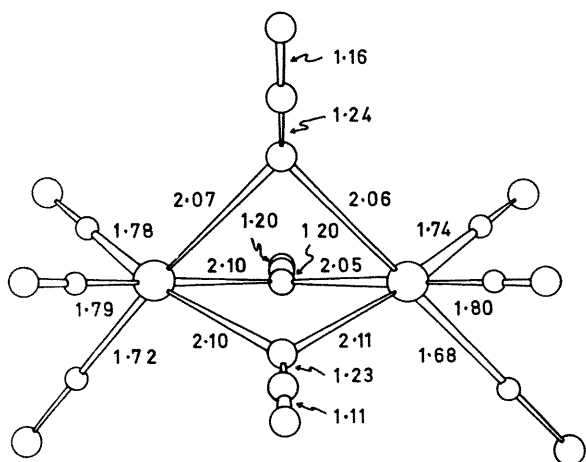


the dimeric anions $[\text{Mn}_2(\text{CO})_6(\text{N}_3)_x(\text{NCO})_{3-x}]^{2-}$ which contain both azide and isocyanate ligands. Mixed isocyanato-azido-complexes are formed also on recrystallizing $\text{Na}[\text{Mn}_2(\text{CO})_6(\text{N}_3)_3]$ or by treating $\text{NEt}_4[\text{Mn}_2(\text{CO})_6(\text{N}_3)_3]$ with carbon monoxide. $\text{Mn}(\text{CO})_5\text{Br}$ and KOCN in ethanol-water at 20° afford the homogeneous tris- μ -isocyanato-complex $[(\text{CO})_3\text{Mn}(\text{NCO})_3\text{Mn}(\text{CO})_3]^{2-}$. Similarly, reaction of $\text{Re}(\text{CO})_5\text{Cl}$ and NaN_3 in tetrahydrofuran at 50° provides colourless $[\text{Re}_2(\text{CO})_6(\text{NCO})_2(\text{N}_3)_2]^{2-}$, which was isolated as the triethylammonium salt. Analogous halogeno-complexes

From the position of $\nu_{\text{as}}(\text{N}_3)$ and $\nu_{\text{as}}(\text{NCO})$ bands azide- and isocyanate-bridges can be clearly distinguished from corresponding terminal ligands (see Table). Azide bridges show higher $\nu_{\text{as}}(\text{N}_3)$ frequencies than terminal azide groups,⁵ whereas ν_{as} absorptions (NCO) of isocyanato bridges appear at lower frequencies than those of monomeric isocyanato-complexes.⁶ The structure (A) is suggested, therefore, for $[\text{Re}_2(\text{CO})_6(\text{N}_3)_2(\text{NCO})_2]^{2-}$, with azide bridging being preferred to isocyanate bonding bridge. In order to elucidate the mode of azide bridging an X-ray structural determination of $\text{NEt}_4[\text{Mn}_2(\text{CO})_6(\text{N}_3)_3]$ was carried out. Crystals of only moderate quality were obtained from an ethanol-water solution and are monoclinic with $a = 10.30$, $b = 10.21$, $c = 21.92$ Å; $\beta = 91.1^\circ$; space group $P2_1/n$; $Z = 4$. Intensity measurements were made by four-circle automatic diffractometer methods (Mo- K_α) and provided 1308 independent reflexions for which $F_{\text{obs}}^2/\sigma(F_{\text{obs}}^2) \geq 3.0$. Patterson, Fourier, and least-squares methods have been used to determine and refine atomic parameters, the present unweighted discrepancy index being 0.10 (all atoms, with the exception of those of the tetraethylammonium cation, have been given anisotropic thermal parameters and there is evidence of cation disordering in the lattice). E.s.d.'s of bond lengths in the anion, the stereochemistry of which is shown in the Figure, average 0.02 Å (Mn-N and Mn-C) and 0.03 Å (N-N and C-O).

The bonding of the three azide groups to the manganese ions is such that the manganese-manganese separation is 2.893 ($\sigma = 0.004$) Å, identical within experimental error to the metal-metal bond length in $\text{Mn}_2(\text{CO})_{10}$ ⁷ and Mn_2 -

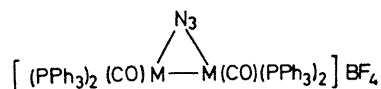
(CO)₈(PEt₃)₂,⁸ the Mn-N-Mn bond angles average 88.6°, again indicative of relatively weak direct metal-metal interaction. The N-N bond lengths in the bridging azide



FIGURE

ligands are scarcely different in a statistical sense but follow a pattern which would have been expected.

An N-diazonium type of azide bridging, where two metals are bridged through the same nitrogen atom, is also found in hexa-azido-dipalladate(II) anion, [(N₃)₂Pd(N₃)₂Pd(N₃)₂]²⁻,⁹ and can be assumed also for other azide bridged complexes. This has been found by treating monomeric azide complexes with oxonium or nitrosyl salts.¹⁰ By this method the complexes (I) and (II) have been obtained from



(I) M = Rh

(II) M = Ir

(Ph₃P)₂M(CO)N₃ and CH₃O⁺BF₄⁻ or NO⁺BF₄⁻, respectively.¹¹

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