New Transition-metal Carbonyl and Nitrosyl Sulphur Complexes

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THE maleonitriledithiolate (*cis*-1,2-dicyanoethylene-1,2-dithiolate) anion[1] (MNT^{2-}) forms complexes with transition metals in high oxidation states and in unusual electronic configurations.[2] The preparations and properties of some derivatives of metal carbonyls and nitrosyls with metal ions in low oxidation states are now reported.

A brick red compound, formulated as

$$\{Ph_3PCH_3\}\{Mn(CO)_4MNT\},$$

formally containing manganese(I), was isolated from the reaction of $Mn(CO)_4Br$ and Na_2MNT in methanol. The compound is monomeric, $\Lambda = 76$ mhos cm.^{2} moles^{-1} in a 10^{-4}M-nitromethane solution (Found: C, 55·6; H, 3·5; N, 5·4; Mn, 9·1. $C_{27}H_{18}MnN_2O_4PS_2$ requires C, 55·5; H, 3·1; N, 4·8; Mn, 9·4%). The infrared spectrum (Table) is also consistent with this formulation.

$[Mo(NO)_2Cl_2]_n$[3] reacts similarly with Na_2MNT in methanol to form a deep green complex, isolated as $\{Ph_4P\}_2\{Mo(NO)_2(MNT)_2\}$, which is also monomeric, $\Lambda = 172$ mhos cm.^{2} moles^{-1} in a 10^{-4}M-nitromethane solution (Found: C, 59·7; H, 3·6; N, 7·1. $C_{56}H_{40}MoN_6O_2P_2S_4$ requires C, 60·3; H, 3·6; N, 7·5%). The infrared spectrum (Table) is in accord with a *cis*-configuration of the nitrosyl groups, the nitrosyl stretching frequencies occurring in the region assigned to co-ordinated "NO^+" groups.[4] The complex formally contains molybdenum in its zero oxidation state. It seems possible that there are two geometrical isomers although no attempt has yet been made to separate them.

The infrared spectral data can be compared with those of their dialkyldithiocarbamate analogues and some halides of similar molecular symmetry. It is seen from the spectra of the molybdenum compounds that the nitrosyl stretching frequencies in the anionic MNT complex are higher than might have been expected since the presence of a negative charge on the metal atom should reduce the symmetric and antisymmetric nitrosyl stretching frequencies by at least 80 cm.$^{-1}$ from the value in $Mo(NO)_2(S_2CNMe_2)_2$.[5] While the dithiocarbamate ligand can function as a weak electron donor, the effect on carbonyl stretching frequencies is small[6] and a similar situation would be expected in the nitrosyl complexes. An explanation of these new results may be that the MNT ligand is functioning as a π-acceptor and so is competing with the nitrosyl ligands for the excess of negative charge. It is more difficult to observe this effect

The carbonyl and nitrosyl stretching frequencies of manganese and molybdeunm complexes

Compound	Solvent	Carbonyl stretching modes				Ref.
$\{Mn(CO)_4MNT\}^-$	$CHCl_3$	2075w	2010vs	1982s	1933m	this work
$Mn(CO)_4S_2CNEt_2$	$CHCl_3$	2091	2019	1996	1953	6
$\{Mn(CO)_4Cl_2\}^-$	Nujol	2040	2002	1969	1915	8
$[Mn(CO)_4Cl]_2$	CCl_4	2104	2045	2012	1977	9
		Nitrosyl stretching modes				
$\{Mo(NO)_2(MNT)_2\}^{2-}$	$CHCl_3$	1742s	1633s			this work
$Mo(NO)_2(S_2CNMe_2)_2$	$CHCl_3$	1770s	1670s			5
$\{Mo(NO)_2Cl_4\}^{2-}$	Nujol	1720	1600			3
$[Mo(NO)_2Cl_2]_n$	Nujol	1805s	1690s	1600w		3

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[2] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1965, **4**, 55, and references therein; S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.*, 1964, **86**, 4594, and references therein.

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[4] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

[5] F. A. Cotton, B. F. G. Johnson, and J. A. McCleverty, to be published.

[6] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 1964, **3**, 1398.

in the manganese carbonyl compounds because of the complexity of the carbonyl stretching modes. Certainly the reduction in all four carbonyl stretching frequencies is *smaller* in the two sulphur complexes on adding a negative charge than for the two chlorides; no definite and rigorous comparison, however, can be made.

It has been suggested[7] that the MNT ligand and its analogues ($[(CF_3)_2C_2S_2]_2$ and $\{Ph_2C_2S_2\}^{2-}$) donate electrons to metals in what are apparently high oxidation states. This is not inconsistent with the ligand having electron accepting properties when the metals are in low oxidation states.

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