Mononitrosylmolybdenum Tris-(*NN*-dialkyldithiocarbamates)

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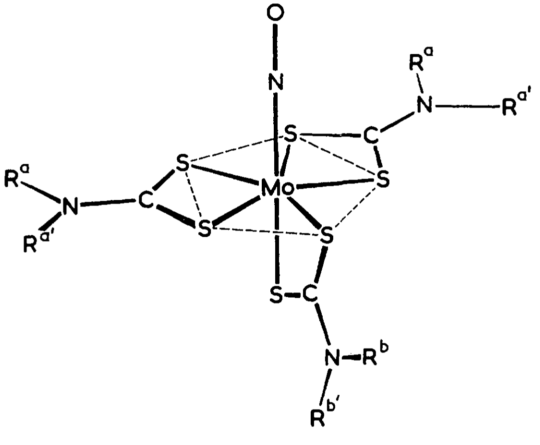
THREE main types of nitrosyl dithiocarbamate complexes are known, *viz.*, (i) the monomeric, five co-ordinate $M(NO)(S_2CNR_2)_2$ (M = V,[1] Fe,[2–4] Ru,[5] or Co[2,3,6]), (ii) the monomeric, six co-ordinate $M(NO)_2(S_2CNR_2)_2$ (M = Cr[7,8] or Fe[7]) and (iii) the monomeric, six co-ordinate $Ru(NO)(S_2CNR_2)_3$.[5] Recently the structure of $Ru(NO)(S_2CNMe_2)_3$ has been established by *X*-ray studies.[9] It is unusual in that one of the dithiocarbamate groups is acting as a monodentate ligand. We now report the preparation of the formally analogous compounds, $Mo(NO)(S_2CNR_2)_3$, (R = Me or Et). In contrast to the ruthenium compounds these contain three chelating dithiocarbamate ligands and may be regarded as seven co-ordinate derivatives of molybdenum(II).



Treatment of $[Mo(NO)Cl_3]_n$[10] with NaS_2CNR_2,$2H_2O$ (R = Me or Et) in acetone gives $Mo(NO)(S_2CNR_2)_3$ as yellow rhombs. Good analytical data have been obtained for these compounds. They are volatile and soluble in organic solvents. In the i.r. spectra of the methyl and ethyl derivatives a strong band observed at 1630 cm.$^{-1}$ is assigned to the N–O stretching vibration. A second broad band in the region 1510—1530 cm.$^{-1}$ is attributed to the C–N stretching vibration.[11] Bands associated with monodentate dithiocarbonate ligands[9] are not observed in either case. The monomeric nature of these compounds was confirmed from mass spectral studies. Parent molecular-ions $[Mo(NO)(S_2CNR_2)_3]^+$ were observed together with ions of the type $[MoS_6C_3N_3R_6]^+$ and $[MoS_6C_3N_3R_n]^+$ (n = 0—6) corresponding to the loss of the NO group and the fragmentation of the co-ordinated dithiocarbamate ligand.

The n.m.r. spectra of these complexes provide the main evidence for the presence of three chelating dithiocarbamate ligands. With the methyl compound four methyl resonances of relative intensities 1 : 2 : 2 : 1 are observed in the region of τ 6·7: this is consistent only with the structure shown. Other possibilities, *e.g.* a structure containing a monodentate S_2CNR_2 group, may be ruled out on this basis. The symmetry of this molecule is low (C_S) and because of the hindered rotation about the C–N bond the methyl groups a and a′ and b and b′ show different chemical shifts. This provides additional evidence for the double bond character of this C–N bond.[12] The ethyl compound shows similar behaviour. The temperature dependence of these spectra is at present under investigation.[13]

One of us (K.H.A.) thanks the Government of Iraq for a maintenance grant.

(*Received, May 28th,* 1968; *Com.* 693.)

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