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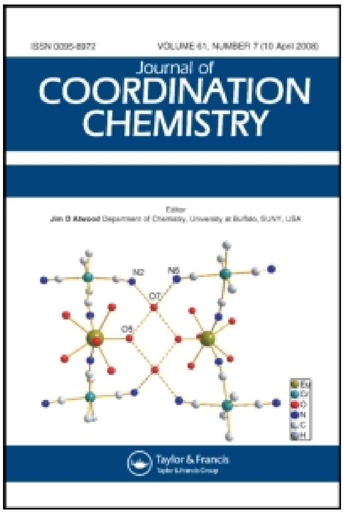

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The Infrared Spectra of some Mono- and Binuclear Oxo-complexes of Molybdenum(IV), -(V), and -(VI); The Assignment of $(LL)_4Mo_2O_3$ Spectra

F. A. Cotton[a]; Douglas L. Hunter[a]; L. Ricard[b]; R. Weiss[b]
[a] Department of Chemistry, Texas A&M University, College Station, Texas [b] Universite Louis Pasteur de Strasbourg, Institut de Chimie, Strasbourg, France

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SHORT COMMUNICATION

The Infrared Spectra of some Mono- and Binuclear Oxo-complexes of Molybdenum(IV), -(V), and -(VI); The Assignment of $(LL)_4Mo_2O_3$ Spectra

F. A. COTTON and DOUGLAS L. HUNTER
Department of Chemistry, Texas A&M University, College Station, Texas 77843

L. RICARD and R. WEISS
Universite Louis Pasteur de Strasbourg, Institut de Chimie, Boite Postale 296 R8 67008 Strasbourg, France

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INTRODUCTION

The assignment of the Mo–O stretching frequencies of oxomolybdenum complexes, especially when other ligands of some complexity are present has proved difficult. In the case of molybdenum(V) compounds of the type $Mo_2O_3(LL)_4$, where LL represents a bidentate ligand, the problem has been especially tedious, and there does not yet appear to be a concensus as to the correct assignment. The spectra of the three compounds, $(dtc)_2MoO$, $(dtc)_2MoO_2$ and $Mo_2O_3(dtc)_4$, where dtc represents $(n\text{-}C_3H_7)_2NCS_2^-$, all of which have recently been structurally characterized by x-ray crystallography[1] are reported here. In addition, some data on related compounds has been taken from the literature. It is then shown that many, though not all, of the previous uncertainties about the $Mo_2O_3(LL)_4$ assignments can now be resolved.

PROCEDURES AND RESULTS

The compounds were all examined as mineral oil mulls using a Perkin-Elmer Model 451 spectrometer and polystyrene film was used for calibration. The spectra in the region of interest are shown in Fig. 1 for two of the $Pr_2^nNCS_2^-$ complexes.

All of the experimental data on $Mo_2O_3(LL)_4$ compounds which will enter into the discussion of the assignments is collected in Table I.

The spectrum of $(Pr_2^nNCS_2)_2MoO_2$ is shown in Fig. 1. The results agree well with those already reported by Moore and Rice[2]. The spectrum of $(Pr_2^nNCS_2)_2MoO$ is virtually identical to that of $(Pr_2^nNCS_2)_2MoO_2$ except for the absence of the two strong Mo–O stretching bands at 882 and 914 cm^{-1} and the presence of a new one at 965 cm^{-1}, of very high intensity. This observation is in excellent agreement with the reported[3] band (962 cm^{-1}) for $(Et_2NCS_2)_2MoO$.

DISCUSSION

The first compound of the type $(LL)_4Mo_2O_3$ for which an assignment of Mo–O stretching bands was

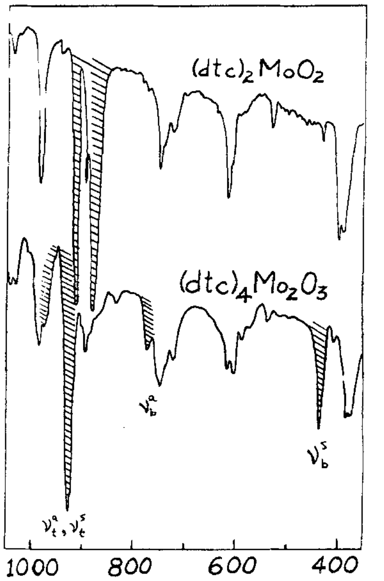
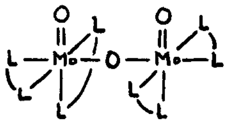


FIGURE 1 The infrared spectra of two of the $(n\text{-}C_3H_7)_2NCS_2^-$ complexes, where dtc represents the dithiocarbamate ligands. Bands assigned to Mo–O stretching are crosshatched. The symbols ν_t^a, ν_t^s, ν_b^a and ν_b^s are explained in the text.

proposed was that in which LL = $C_2H_5OCS_2^-$[4a]. In the light of subsequent work the assignment then proposed seems to be incorrect. We believe that it is now possible to make a generally valid assignment for the entire class of $(LL)_4Mo_2O_3$ compounds. Four compounds will be considered in order to do so. Two of these have an essentially cis relationship in the O=Mo—O—Mo=O group, 1; these are the compounds[1 4] with LL = $(n\text{—}C_3H_7)_2NCS_2^-$ and $C_2H_5OCS_2^-$. It should be noted that the O=M—O—M=O group in the cis structure it is not necessarily completely planar[4a] and in general will not be; in other words, its symmetry may be only C_2 and not C_{2v}.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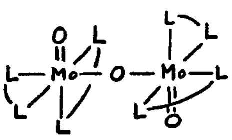
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The other two compounds, in which LL = $(C_2H_5O)_2PS_2^-$ and $(C_6H_5O)_2PS_2^-$ have a trans relationship,[5] 2.

For either type of $(LL)_4Mo_2O_3$ compound four fundamental Mo–O stretching fundamentals are expected. For the terminal Mo–O bonds there should be symmetric and antisymmetric modes, ν_t^s and ν_t^a. Since the two terminal Mo–O oscillators are well separated, the coupling constant is likely to be small, and interaction through the kinetic energy matrix (G matrix) should be virtually negligible. At the same time, there does not appear to be any reliable basis for predicting whether the net result, however small, will result in $\nu_t^s > \nu_t^a$ or vice versa.

For the symmetric and antisymmetric stretching modes of the Mo—O—Mo bridge system, ν_b^s and ν_b^a, four factors must be considered. (1) The bridge Mo—O bonds are certainly weaker than the terminal Mo—O bonds, according to the observed bond lengths; thus bridge bond stretching frequencies ought to be lower than terminal ones. (2) Since ν_b^s must involve only motion of the Mo atoms, whereas ν_b^a is a motion mainly of the light oxygen atom, kinetic energy considerations, in themselves, would strongly require $\nu_b^a \gg \nu_b^s$. (3) It seems very probable that there will be a positive bond stretching interaction constant in the Mo–O–Mo system, which will tend to make $\nu_b^s > \nu_b^a$. However, the mass (kinetic energy) effect should greatly outweigh the effect of an interaction constant of reasonable magnitude,[5b] and thus the inherent tendency of the Mo–O–Mo group will be to have $\nu_b^a > \nu_b^s$. (4) Finally, there will be some interactions between the bridge and terminal modes; the consequences of this will probably be of small magnitude but uncertain direction.

Despite the indefiniteness of some of the foregoing factors, the possibility of reaching a reasonably firm assignment, at least in the main features, is fairly good. This is in part because there is much empirical data on simpler systems, containing only bridge or only terminal Mo–O bonds, and in part because the availability of both cis and trans Mo_2O_3 systems, 1 and 2, can be put to advantage.

To interpret the data, (Table I) we begin by noting that for the $(RO)_2PS_2$ compounds, only ν_t^a and ν_b^a should be observed in the infrared. For these compounds, there are, in fact, just two bands, and their assignments, as indicated in the Table, are straightforward.

TABLE I
Metal–oxygen stretching bands (cm^{-1}) in the infrared spectra of $(LL)_4Mo_2O_3$ compounds

Compound	ν_t^a	ν_t^s	ν_b^a	ν_b^s
$(Pr_2^nNCS_2)_4Mo_2O_3$	975	930	770	447
$[(EtO)_2PS_2]_4Mo_2O_3$[a]	981	*b*	782	*b*
$[(PhO)_2PS_2]_4Mo_2O_3$[a]	972	*b*	785	*b*
$(EtOCS_2)_4Mo_2O_3$		954	760	438

[a]Data from R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 1702 (1970).

[b]Symmetric modes not observed in ir due to center of symmetry.

From this point it is then easy to assign both of the bridge modes, ν_b^a and ν_b^s in the other molecules, since each has a band in the 730–785 cm^{-1} range which must be due to ν_b^a, thus leaving the observed bands in the range 430–450 cm^{-1} to be assigned to ν_b^s.

In connection with these assignments of ν_b^a and ν_b^s, two points are worth noting. First, the ratio of the intensities of the two bands is quite variable. As shown in Fig. 1, ν_b^s is about twice as intense as ν_b^a for the $(dtc)_4Mo_2O_3$ case, whereas in $(EtOCS_2)_4Mo_2O_3$ (see ref. 4 for the spectrum) the opposite is true. The value of $\nu_b^a - \nu_b^s$ is relatively large (~ 320 cm^{-1}) in these two cases, and the Mo–O–Mo chains are known to be essentially linear. This is in accord with the ideas of Wing and Callahan.[6]

We turn now to the terminal Mo–O stretching modes, where the situation is still ambiguous in certain respects. Clearly, for the $(RO)_2PS_2$ compounds the strong band at 972 or 981 cm^{-1} must be ν_t^a. For the other compounds, which we may assume to contain O=Mo–O–Mo=O systems with essentially

C_{2v} symmetry and nearly parallel O=Mo groups, both ν_t^a and ν_t^s should be infrared-active. However, the intensity of ν_t^s might be expected to exceed that of ν_t^a, since the necessary transition moment for ν_t^s will be essentially in the direction of the Mo–O bond moments whereas for ν_t^a a transition moment must be generated approximately perpendicular to the mean direction of these bond moments. On this basis, we think it very reasonable to assign the strong band in the dtc compound at 930 cm^{-1} to ν_t^s and the much weaker band at 975 cm^{-1} to ν_t^a. The fact that the latter frequency agrees well with the mean (976 cm^{-1}) of the ν_t^a frequencies in the $(RO)_2PS_2$ complexes lends some support to this assignment.

Evidently, the very strong band at 954 cm^{-1} in the $EtOCS_2$ compound is due to ν_t^s, and ν_t^a is not observed. It could, if quite weak, be obscured under the band at about 995 cm^{-1} (See ref. 4b).

The $Mo_2O_3Cl_8^{4-}$ anion[7] would make an excellent model compound, and it was originally hoped to employ it in this way. Its reported spectrum has bands at 983, 958, 735 and 516 cm^{-1} which fit in well with the assignments proposed here, assuming a cis structure, Unfortunately, our attempts to reproduce the literature results have been less than encouraging. Only small amounts of material resembling in appearance the reported $[(C_2H_5)_4N]_4[Mo_2O_3Cl_8]$ have been obtained, and not reproducibly. The ir spectra were similar to but not identical with those reported. However, in all cases, analytical data were wholly unsatisfactory. In our experience, salts of $Mo_2O_3Cl_8^{4-}$ cannot be regarded as established compounds.

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