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Complexes of Dithiobenzoic Acids. V. Observations on the Nature of the Molybdenum–Sulfur Bond in Tetrakis(dithiobenzoato)Molybdenum(IV) Complexes

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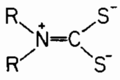
Interpretations of data from infrared, visible-ultraviolet, and ^{13}C NMR spectra lead to the conclusion that there is extensive covalent bonding in dithiocarboxylates, 4, of eight-coordinated molybdenum(IV), $[Mo(4)_4]$, and suggest the presence of metal-to-ligand π backbonding, in contrast to the bonding in analogous dithiocarbamate complexes. Some d–d bands have been observed in the latter compounds, but in the dithiocarboxylates the d–d transitions are buried beneath intense low energy charge transfer bands, implying very efficient mixing of metal and ligand orbitals. The first CT band (at least) is most likely metal(xy)-to-ligand(π^*).

Introduction

Although there is much interest in molybdenum–sulfur compounds containing four- and six-coordinate molybdenum because of the relevance of such compounds in metallobiomolecules (such as the Fe–Mo cofactor in nitrogenase), there is much less known of the biologically unimportant and relatively recent eight-coordinate Mo–S compounds. The first report of such a compound appeared in 1968 [1] when $[Mo(1,\ R = CH_3)_4]$ was prepared from $Mo(CO)_6$ and tetramethylthiuramdisulfide. Soon additional dithiocarbamate eight-coordinate species were prepared [2] by CS_2 insertion into $Mo(NR_2)_4$ compounds. Similar complexes containing xanthate, *2*, [3, 4], thioxanthate, *3*, [5], and dithiocarboxylates, *4*, [6, 7], soon followed. There have been (a) three x-ray structural studies, *viz.*, $[Mo(1,\ R = C_2H_5)_4]$ [8], $[Mo(5a)_4]$ [9], and $[Mo(5b)_4]$ [10]; (b) magnetic measurements [7, 11] which showed these compounds to be diamagnetic when free of impurities; (c) electronic spectral studies [5–7, 12]; (d) electrochemical studies [5, 13]; and (e) ^{13}C NMR studies of a series of complexes of *5* in which the aromatic ring has been substituted with a variety of groups [14].



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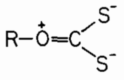

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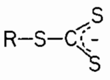

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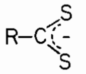

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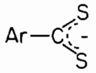

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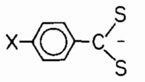

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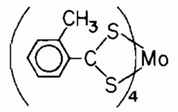

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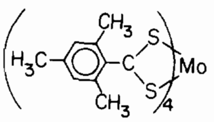
X = H (a), CH_3 (b), CH_3O (c), Cl (d), F (e), C_6H_5 (f), CHO (g), C_6H_5CO (h), CH_3CO (i), $(n\text{-}C_4H_9)_2N$ (j)



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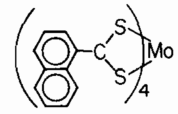

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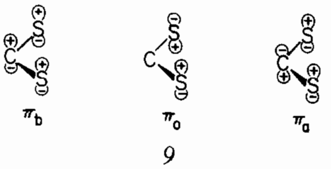

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It is expected that as metallic oxidation state increases the covalent nature of metal–ligand bonds likewise increases. Thus it was surprising to find that after the successful use [15] of a ligand field model for the interpretation of the electronic spectra of the *penta*valent eight-coordinate dithiocarbamate complexes, $[M(1)_4]^+$ (M = Mo, W), an analogous

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point charge model [12] did not work well with *tetra*valent eight coordinate dithiocarboxylate compounds, [Mo(*4*)$_4$], and that these latter species seemed much more covalent than the former. This paper explores this apparent anomaly by looking at IR, NMR, and electronic spectral data to see what they reveal of the nature of the bonding in such Mo–S_8 species and what role (if any) can be deduced for π bonding involving the molybdenum.

Experimental

Thirteen molybdenum complexes of dithiobenzoic acids, [Mo(*5*)$_4$], *6–8*, were prepared, as already described [7], from $MoCl_4(CH_3CH_2CH_2CN)_2$. Infrared spectra were obtained on a Perkin-Elmer 621 using nujol mulls (4000–700 cm^{-1}, NaCl; 700–200, CsI). Some dithioacids were examined as neat oils between CsI plates. Ultraviolet-visible spectra were recorded on a Cary 14 spectrophotometer, in chloroform solutions (10^{-3}–10^{-6} *M*). The proton noise decoupled ^{13}C NMR spectra were obtained at ambient temperature on a JEOL FX-100 spectrometer using the solvent $CDCl_3$. Tetramethylsilane served as the internal standard. Pertinent data are collected in Tables I and II.

Discussion

The possibility of extensive covalent bonding in the molybdenum dithiocarboxylates and in particular for π backbonding by the metal, can be envisioned in a simple non-rigorous fashion. In the three 1,1-dithioacid complexes whose structures have been determined by X-ray diffraction [8–10] (*vide supra*), the C–S–Mo angles are all very near 90°, implying (in the valance bond formalism) that sulfur uses nearly pure *p* orbitals in both the Mo–S and C–S sigma bonds. This leaves π orbitals directed perpendicular to the chelate ring. The two sulfur 3pπ AOs and the carbon 2pπ AO of the CS_2^- group combine into three MOs: π_b, π_o, π_a (see *9*). These group orbitals, of B_1 symmetry in D_{2d} and 2/3 full with four electrons, can interact with the filled metal xy (B_1) orbital. When this occurs the molybdenum may become involved in pi backbonding. Thus π backbonding is possible, but does it in fact occur?

There is some indirect evidence from infrared data for a high degree of covalency and for π back donation in the Mo(IV)-dithiocarboxylates. For example, in the series of complexes Mo[*5*(*a–i*)]$_4$ the frequency due primarily to the phenyl-carbon stretch is found to increase an average of 23 cm^{-1} for 10 complexes, from 1240–1270 cm^{-1} for the ligand acids to 1260–1290 cm^{-1} for the complexes (Table I). On the other hand, in the cases of the three complexes *6*, *7*, and *8*, where steric factors should prevent conjugation or delocalization of charge from the -CS_2Mo, chelate ring portion of the molecule into the aromatic ring, the frequency changes are +10, –10, and –5 cm^{-1}, respectively. The phenyl–carbon bond, which links the two rings (aromatic and chelate), would be expected to increase in strength if there were an electron density increase in the CS_2 portion of the molecule and assuming the two rings are coplanar. Thus if there were only sulfur-to-metal sigma donation (and especially if there were in addition sulfur-to-metal π donation) this bond would be expected to weaken correspondingly. However, if there were metal-to-sulfur π back donation the bond order should increase and be reflected in a higher stretching frequency. If there were not coplanarity of the two rings this π electron communication and bond strengthening would not occur. Thus the available infrared data suggest (but do not prove) that the diammagnetic d^2 molybdenum is engaged in π backbonding.

The electronic spectra of the complexes [Mo(*4*)$_4$] [6, 7, 12], [Mo(*1*)$_4$] [12] and [Mo(*3*)$_4$] [5] suggest a higher degree of covalency in the metal–sulfur bonds than is found in any other eight-coordinate Mo(IV) species, and of these the ligands *3* and *4* seem to exhibit the greatest covalency. The visible-UV bands [7] of all of the dithiobenzoate complexes may be divided into three categories: (a) highly intense (log $\epsilon \sim 4.7$–5.0) absorptions (usually two) in the 27–34 kK region, due most likely to internal ligand ($\pi \rightarrow \pi^*$) transitions, only slightly shifted from their positions in both the ligand acids and anions; (b) up to six, but usually four, intense (log $\epsilon \sim 3.6$–3.9) absorptions in the 11–25 kK range, at least one of which is due to an n $\rightarrow \pi^*$ transition within the CS_2 moiety, with the others most likely being charge transfer transitions, although it is not possible to rule out some bands of *d–d* origin (such as the shoulders at ~13 kK and ~22–23 kK) since these transitions could borrow intensity from nearby strong CT bands; and (c) a much weaker band below 11 kK, not easily observed [16] because of the intense CT band at ~12 kK, and probably due to the first *d–d* transition.

What is most noteworthy about these spectral data is that the charge transfer transitions occur at such low frequencies, in marked contrast to the dithiocarbamate complexes where two *d–d* transitions are observed [12] between 10 and 15 kK and where the intense CT bands begin above ~17 kK. It should be noted that we [17] found no absorptions in the 7–18 kK range for several Ti(IV) and Sn(IV) complexes of dithiocarboxylates. These results are explicable in terms of some extended Huckel calculations made by Nieuwpoort [12, 18] for [Mo(*1*, R = H)$_4$] and [Mo(*4a*, R = CH_3)$_4$], which showed that

TABLE I. Phenyl-carbon Stretching Frequencies (cm^{-1}) for Free Ligand Acids and their Molybdenum Complexes.

Compound[a]	Frequency	Change	Compound	Frequency	Change
5a	1240 1270	+30	*5h*	1240 1275	+35
5b	1255 1275	+20	*5i*	1255 1265	+10
5c	1260 1280	+20	*5j*	1270 1290	+20
5d	1245 1272	+27	*6*	1250 1260	+10
5e	1260 1275	+15	*7*	1260 1250	−10
5f	1245 1274	+29	*8*	1240 1235	−5
5g	1240 1260	+20			

[a] The value listed first is for the acid and the second value is for the molybdenum complex.

in the former the metal has a lower charge (+1.05) than in the latter (+1.34), in agreement with the greater electron donating character of the dithiocarbamate compared to the dithiocarboxylate. These calculations also showed that the coefficient of the metal xy orbital in the HOMO for the former (0.88) is lower than for the latter molecule (0.95) and that the LUMO in the former has only 50% ligand character compared to 98% in the latter. These findings not only help explain the low frequency intense absorptions near 12 kK in the dithiocarboxalate complexes but they suggest that the CT bands of the complexes *5–8* are metal (xy)-to-ligand(π^*) in character.

Additional experimental support for this proposed pi backbonding comes from ^{13}C NMR data. As shown by the data in Table II, the ^{13}C resonance of the CS_2 carbon is shifted strongly upfield (~37 ppm) in eight complexes from its position in the ligand anion. The upfield shift of this same resonance from ligand acid to complex (~9 ppm) also reflects the enhanced shielding of the chelate ring carbon. The phenyl carbon, C-1, is also more shielded in the complex than in the salt (average $\Delta\delta \simeq -13$ ppm), but much less so in the complex compared to the acid (average $\Delta\delta = -3$ ppm). Of course the possibility that at least some of the shielding effect evidenced upon complexation arises from nonbonding (paramagnetic) contributions to the chemical shift cannot be ruled out.

TABLE II. ^{13}C Chemical Shifts (ppm) of Dithiobenzoic Acids, Their Tetraalkylammonium Salts and Their Molybdenum(IV) Complexes.

Compound[a]	Chemical shift C-1	C-2	C-4	CS_2
5a[b]	144.7	126.6	132.0	224.5[c]
	153.4	126.7	128.7	253.6
	140.8	123.1	132.8	216.0
5b	140.9	126.9	144.3	224.3
	150.4	126.6	138.7	252.3
	138.9	123.1	143.8	215.5
5c	136.5	129.3	164.2	222.0
	145.5	128.8	161.1	251.0
	135.1	125.1	165.0	214.4
5e[b]	141.0	128.9	165.3	222.1[c]
	149.1	128.8	163.8	251.1
	137.4	125.4	166.3	214.2
5f	141.9	126.8	145.9	223.8
	151.7	127.4	140.7	252.1
	139.7	123.6	145.3	214.6
5g	158.8	126.8	135.3	251.6
	143.4	123.5	138.7	214.6
5h	145.5	126.5	140.9	224.0
	157.1	126.3	137.9	252.5
	142.3	123.5	140.8	214.7
5i	146.0	126.9	139.7	223.9
	157.4	126.3	136.2	252.2
	142.8	123.3	139.7	214.9

[a] The three rows of data for each listed ligand are for the ligand acid, the tetraalkylammonium salt of that acid, and the molybdenum(IV) complex. [b] The methyl ester of the ligand acid was used in place of the less stable acid. [c] Corrected for the downfield shift due to the methyl group.

In sum, however, the following conclusions can be drawn:

1. The eight-coordinated dithioacid, particularly the dithioarylacid complexes of Mo(IV), appear to possess extremely covalent bonds with more effective mixing of metal and ligand orbitals than occurs in dithiocarbamate complexes. The dithiocarbamates are 'harder' ligands than dithiocarboxylates, probably due to a predominating resonance structure in the former ligands bearing a positive nitrogen double bonded to the dithiocarbon (see *1*) whereas in the latter ligands the predominating resonance structure is most likely that shown in *4*.
2. The *d–d* transitions of the dithiocarboxylate complexes of spin-paired d^2 Mo(IV) are generally buried beneath low energy intense CT bands, implying very efficient mixing of metal and ligand orbitals.
3. The first CT band seems to be primarily metal (π, perhaps 90% xy)-to-ligand (π^*, almost pure ligand group π).

4. The molybdenum is probably involved in some pi backbonding with the dithioacids, in which the filled xy metal orbital has combined with the partially filled ligand group (π^*) orbitals.

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