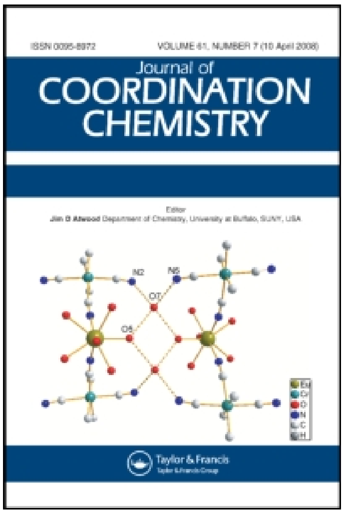

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COMPLEXES OF DITHIOBENZOIC ACIDS. I. PREPARATION AND PROPERTIES OF A SERIES OF MOLYBDENUM(IV) COMPOUNDS

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To cite this Article Roberie, T. , Hoberman, A. E. and Selbin, J.(1979) 'COMPLEXES OF DITHIOBENZOIC ACIDS. I. PREPARATION AND PROPERTIES OF A SERIES OF MOLYBDENUM(IV) COMPOUNDS', Journal of Coordination Chemistry, 9: 2, 79 — 87

To link to this Article: DOI: 10.1080/00958977908076510

URL: http://dx.doi.org/10.1080/00958977908076510

J. Coord. Chem.
1979, Vol. 9, pp. 79-87

COMPLEXES OF DITHIOBENZOIC ACIDS. I. PREPARATION AND PROPERTIES OF A SERIES OF MOLYBDENUM(IV) COMPOUNDS

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(Received August 10, 1978)

A new, simpler, more general and dependable method of synthesizing dithiocarboxalato complexes of molybdenum(IV) is reported. It involves reaction of $MoCl_4 \cdot (CH_3CH_2CH_2CN)_4$ with the acid form of the sulfur ligand. Thirteen Mo(IV) complexes are reported, 11 of which are new compounds and 5 of which contain newly synthesized dithiocarboxylato ligands. All ligands were prepared as the acids and converted to tetraalkylammonium salts for characterization. Infrared and visible–ultraviolet spectral data for the complexes are detailed.

INTRODUCTION

Although the chemistry of dithiocarbamate and xanthate complexes of molybdenum has been investigated in some detail,[1] only three well characterized dithiocarboxylato complexes seem to have been reported. In 1974, Piovesana and Sestili[2] reported the preparation, in low yields (20–30%), of three tetrakisdithiocarboxylatomolybdenum(IV) complexes. They used tetraalkylammonium salts of $MoCl_6^{3-}$ and the acids of the following bidentate ligands as starting materials: $C_6H_5CS_2^-$, p-$CH_3OC_6H_4CS_2^-$ and $C_6H_5CH_2CS_2^-$. Two other analogous compounds containing p-$CH_3C_6H_5CS_2^-$ and 2-naphthoylCS_2^- have been reported,[3] but were not characterized, not even with analytical data; and the color reported for one of them (the *p*-toluoyl compound) suggests to us that the product was at best impure.

We were interested in studying a series of such molybdenum-sulfur complexes in which substituents on the aromatic ring were varied; and so we developed and report here a new method of preparing dithiocarboxylato complexes which is much simpler, more general and more dependable than the Piovesanna-Sestili method and which affords much higher yields.

We have prepared 13 Mo(IV) complexes, 11 of which are new and 5 of which contain new dithiocarboxylato ligands prepared for the first time in this study. Since the ligand acids were generally not very stable, particularly in the air, all of the acids were converted to tetraalkylammonium salts for easier characterization and eleven of those salts are new compounds also. However, it was the acids which were used as starting materials for the preparation of the molybdenum complexes.

The complexes reported here are all of the general formulation, $Mo(S_2C\text{-}X)_4$, where X, the name of the ligand acid, and its abbreviation used by us are as follows:

1) C_6H_5, dithiobenzoic acid, dtbH;

2) p-CH_3-C_6H_4, *p*-dithiotolulic acid, *p*-dttH;

3) o-CH_3-C_6H_4, *o*-dithiotolulic acid, *o*-dttH;

4) p-$CH_3OC_6H_4$, *p*-methoxydithiobenzoic acid, mdtbH;

5) p-Cl-C_6H_4, *p*-chlorodithiobenzoic acid, cdtbH;

6) p-F-C_6H_4, *p*-fluorodithiobenzoic acid, fdtbH;

7) p-C_6H_5-C_6H_4, *p*-phenyldithiobenzoic acid, phdtbH;

8) p-CHO-C_6H_4, *p*-formyldithiobenzoic acid, fordtbH;

9) p-C_6H_5CO-C_6H_4, *p*-benzoyldithiobenzoic acid, bendtbH;

10) p-$CH_3COC_6H_4$, *p*-acetyldithiobenzoic acid, acdtbH;

11) p-$(n\text{-}C_4H_9)_2N$-C_6H_4, *p*-N,N-dibutylaminodithiobenzoic acid, badtbH;

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12) 2,4,6-$(CH_3)_3$-C_6H_2, 2,4,6-trimethyldithiobenzoic acid or dithiomesitoic acid, dtmesH; and

13) 1-$C_{10}H_7$, 1-dithionaphthoic acid, dtnapH.

EXPERIMENTAL

Unless otherwise noted, all chemicals and solvents were reagent grade and were obtained commercially.

Bromobenzene, *p*-bromoanisole, 1-bromo-4-fluorobenzene, bromomesitylene, *p*-bromotoluene, *o*-bromotoluene, and 1-bromonaphthalene were distilled under nitrogen (either at atmospheric or under reduced pressure) from calcium hydride and then stored over 4A molecular sieves. 1-Bromo-4-chlorobenzene and 4-bromobiphenyl were used as received. *p*-Bromo-N,N-dibutylaniline (b.p. 135–137°C at 1.0 mm Hg), prepared by a procedure similar to that of Bullman, Radike, and Munday,[4] was distilled from calcium hydride under reduced pressure and stored over 4A molecular sieves.

The ethylene acetal of *p*-bromobenzaldehyde (b.p. 85°C at 0.15 mm Hg) and the ethylene ketals of *p*-bromoacetophenone (b.p. 72°C at 0.15 mm Hg) and *p*-bromobenzophenone (b.p. 137–139°C at 1.0 mm Hg) were prepared by a standard procedure.[5] Because these crystalline derivatives are hygroscopic, they were stored in a vacuum desiccator over phosphorous pentoxide until needed.

Tetrachlorobis(butyronitrile)molybdenum(IV) was prepared according to a previously published method.[6]

Tetrahydrofuran (THF) was distilled under nitrogen from sodium-benzophenone prior to use. Benzene was dried by distillation from sodium-benzophenone under nitrogen and subsequently stored in a dry box. Carbon disulfide was dried by distillation under nitrogen from phosphorous pentoxide.

Silica gel HF-254 (Brinkmann Instruments, Inc., Westbury, N.Y.) was TLC grade with average grain size 10–40μ. Activated alumina (Matheson, Coleman, Bell) was chromatographic grade (80–325 mesh).

In the synthesis of the molybdenum complexes, the molybdenum and dithioacid solutions were prepared and mixed in a dry box under anhydrous, oxygen-free nitrogen. The refluxing of the resulting reaction mixture was conducted outside the dry box under nitrogen.

Infrared spectra were recorded on a Perkin Elmer 621 using nujol mulls (4000–700 cm^{-1}, NaCl; 700–200, CsI). The IR spectra of some dithioacids were recorded as neat oils between CsI plates. Ultraviolet–visible spectra were recorded on a Cary Model 14 recording spectrophotometer in chloroform solutions (10^{-3}M–10^{-6}M). Melting and/or decomposition points were obtained from thermograms recorded on a DuPont Model 900 thermal analyzer.

C, H, and N analyses were carried out by our own staff employing standard commercial analyzers. Mo and S analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Because of their sensitivity to air oxidation, the dithioacids were not analyzed. However, their corresponding tetraalkylammonium salts were prepared and analyzed since they were found to be extremely stable toward air oxidation.

Preparation of the Dithioacids (X-CS_2H) where X = phenyl, p-tolyl, o-tolyl, p-anisyl, 1-naphthyl, 4-fluorophenyl, 4-chlorophenyl, 2,4,6-mesityl, and 4-biphenyl

The dithioacids were prepared in high yields (70–80%) by the addition of carbon disulfide to the appropriate Grignard reagent at 0°C in THF under a dry nitrogen atmosphere. The acids were prepared and purified by the following method.

To a solution of Grignard reagent, at 0°C, prepared from 4.11×10^{-2} mol of aryl bromide and 6.17×10^{-2} mol of Mg turnings in 100 ml of THF was added 5.0 ml (8.28×10^{-2} mol) of carbon disulfide. After standing for 3 hours at room temperature, the dark red solution was decanted from the excess Mg. The THF was removed under vacuum, ethyl ether (80 ml) added to the residue, and the dithioacid liberated by the addition of 80 ml of ice-cold 6*M* HCl. The colored (violet to red-violet) ether layer was then extracted with 100 ml of an ice-cold 0.4*M* sodium hydroxide solution. The aqueous sodium salt solution (filtered to remove any precipitate) was acidified with ice-cold 6*M* HCl, the liberated dithioacid extracted with ether, and the extraction with sodium hydroxide repeated. The liberation of the acid and extraction with sodium hydroxide was repeated a third time. The acid was liberated once more with the final ether extract being dried over anhydrous magnesium sulfate for two minutes. The mixture was then filtered, the ether removed under vacuum, and the acid dried for three hours under vacuum at room temperature.

Preparation of p-(N,N-dibutylamino)dithiobenzoic acid (badtbH)

This acid was prepared by the previous Grignard method. In the hydrolysis of the Grignard product and in the subsequent neutralization-extraction procedure, 1*M* HCl was used instead of 6*M* HCl in order to avoid formation of the amine hydrochloride which is soluble in water (violet solutions) and which, if formed, will cause problems during the extraction procedure. Also, during the extraction of the colored (dark reddish-brown) ether layer with aqueous base, the sodium salt of the acid may oil out with the concurrent formation of three separate layers. Addition of 50 to 100 ml of water at this point will eliminate the problem. Otherwise the acid was obtained and dried as described previously. The acid is a crystalline brown solid with a melting point near room temperature. *Yield:* ca. 63%.

Preparation of p*-formyldithiobenzoic acid (fordtbH)*

9.41 g (4.11 x 10^{-2} mol) of the ethylene acetal of *p*-bromobenzaldehyde and 2.18 g of ethylene dibromide in 60 ml of THF were added dropwise to 2.0 g (8.22 x 10^{-2} mol) of Mg turnings in 50 ml of THF. A crystal of iodine was added to initiate the reaction. The rate of addition of the acetal solution was such that the THF never boiled. (When the THF boiled, a considerable amount of white precipitate formed and low yields (0–10%) of the Grignard were obtained.) The yellow Grignard solution was stirred for one hour after the last of the acetal solution had been added. The solution was then cooled to 0°C and 5 ml of carbon disulfide added dropwise with stirring. The dark red solution sat in the ice bath three hours before being decanted from the excess Mg. The THF was removed, ethyl ether (80 ml) added to the residue, and the acid liberated with 80 ml of ice cold 1*M* HCl. The colored ether layer was extracted with 80 ml of an ice-cold 0.4*M* sodium carbonate solution. The dissolved ether was removed from this aqueous salt solution on a rotary evaporator at 50°C. The filtered salt solution was added dropwise with stirring to 100 ml of a 0.3*M* zinc chloride solution. The yellow zinc salt precipitated immediately. The slurry was cooled in an ice bath and the pH of the mixture adjusted to one (pH paper) by the dropwise addition of ice-cold 6*M* HCl. The mixture was then stirred overnight at room temperature. The zinc salt was collected by filtration and stirred with 100 ml of conc. HCl for 2 to 3 minutes. The crude acid was collected by filtration and added to 80 ml of a warm (50°C) 0.4*M* sodium carbonate solution. When no more acid appeared to go into solution, the mixture was filtered. The filtrate was cooled in an ice bath and the dithioacid liberated with ice-cold 6*M* HCl. The liberated acid was collected by filtration, washed with 50 ml of cold water, and dried under vacuum for 6 hours at room temperature. The acid, a tan powder, was very slightly soluble in almost all common organic solvents. *Yield:* 60%.

Preparation of p*-benzoyldithiobenzoic acid (bendtbH) and* p*-acetyldithiobenzoic acid (acdtbH)*

These acids were prepared by the procedure used in the synthesis of *p*-formyldithiobenzoic acid. The Grignard solutions may be refluxed since no precipitate forms as it did with the acetal. *Yield:* acdtbH, 64%; bendtbH, 69%.

Sodium Dithiobenzoates

An etheral solution of dithioacid, obtained after the hydrolysis of the Grignard-CS_2 product, was extracted with 80 ml of aqueous 0.25*M* Na_2CO_3. Dissolved ether was removed (at 40°C) from the brown aqueous salt solution on a rotary evaporator. The solution was then filtered, the water removed under vacuum, and the crude salt dried under vacuum at 70°C for 3 hours. The crude salt was then added to 125 ml of boiling 95% ethanol. After a few minutes, the insoluble Na_2CO_3 was filtered off, the solution boiled down to 50 ml, and an equal volume of benzene added. This reduction of volume and addition of benzene was continued until crystals appeared. The solution was then allowed to cool to room temperature. After 3 hours, the crystals were collected by filtration and then dried under vacuum at 80°C for six hours. The sodium salts prepared as above were as follows: Na(dtb) (red-orange plates), Na(fdtb) (red crystals), Na(dtt) (bright red needles), and Na(mdtb) (red-orange crystals).

The sodium salt of acdtbH was obtained as a green powder by removal of the ethanol under vacuum and was used as such since attempts at recrystallization yielded a brown tar.

Tetraethylammonium Dithiobenzoates

2.47 g (1.49 x 10^{-2} mol) of Et_4NCl in 30 ml of chloroform were added to 1.49 x 10^{-2} mol of a sodium dithiobenzoate suspended in 60 ml of chloroform. The chloroform was heated to a gentle boil for two minutes. The resulting reddish-brown solution was cooled in an ice-bath for a few minutes and then filtered to remove the suspended NaCl. Chloroform was removed and the residue dried under vacuum for 3 hours. The crystalline brown solid was then added to 80 ml of boiling THF. Methanol was added dropwise until all the solid had dissolved. The THF was then boiled down until crystals began to form along the sides of the beaker. At this point, enough methanol was added to just redissolve the crystals. The solution was then removed from the heat. After four hours, the crystals were collected by filtration, were washed with 50 ml of ethyl ether, and were dried under vacuum at room temperature for six hours. Typical yield: 81%.

The tetraethylammonium salts of acdtbH and fdtbH were prepared as above but were recrystallized from acetone-ethyl ether. The salts have a tendency to oil out, but by the careful adjustment of the acetone-ether ratio followed by cooling in an ice bath, crystals can be obtained.

Tetrapropylammonium Dithiobenzoates

An etheral dithioacid solution, obtained after the hydrolysis of the Grignard-CS_2 product, was extracted with 80 ml of aqueous 0.25*M* Na_2CO_3. The dark brown aqueous salt solution was freed of dissolved ether as previously described. The filtered solution was then added dropwise to an ice-cold solution of 10.9 g (4.11×10^{-2} mol) of tetrapropylammonium bromide in 100 ml of water. The crystals were then collected by filtration, washed with 50 ml of cold water, and dried under vacuum. The salt of the acids phdtbH, *o*-dttH, dtnapH, and dtmesH were recrystallized from THF-methanol as previously described. The salts of the acids amdtbH and fordtbH were recrystallized from acetone-ether as previously described. The salt of bendtbH was recrystallized from water. The salt of cdtbH was not recrystallized. Typical yield: 75.0%.

Preparation of Mo(dtb)$_4$, Mo(p-dtt)$_4$, Mo(o-dtt)$_4$, Mo(mdtb)$_4$, and Mo(phdtb)$_4$

1.00 g (2.66×10^{-3} mol) of tetrachlorobis(butyronitrile)molybdenum(IV) in 100 ml of warm benzene was added to 1.06×10^{-2} mol of the appropriate dithioacid in 30 ml of benzene. After one hour of refluxing, the solution had changed from its initial greenish-brown color to either a dark blue-violet (Mo(dtb)$_4$, Mo(*p*-dtt)$_4$, and Mo(*o*-dtt)$_4$) or a dark emerald green (Mo(mdtb)$_4$ and Mo(phdtb)). The heating was discontinued and the hot solution was poured into a 250 ml beaker containing activated charcoal. The mixture was heated to boiling before being filtered. The dark blue-violet or dark green solution was now boiled down to about 30 ml before being allowed to sit undisturbed for 24 hours. The crystals were then collected by filtration and recrystallized once more before finally being dried under vacuum at 78°C for twelve hours. *Yields:* Mo(dtb)$_4$, 1.46 g (77.2%); Mo(*p*-dtt)$_4$, 1.53 g (76.4%); Mo(*o*-dtt)$_4$, 1.62 g (79.6%); Mo(mdtb)$_4$, 1.77 g (80.2%); Mo(phdtb)$_4$, 1.90 g (70.5%).

Preparation of Mo(fdtb)$_4$, Mo(acdtb)$_4$ and Mo(dtnap)$_4$

To 1.00 g (2.66×10^{-3} mol) of tetrachlorobis(butyronitrile)molybdenum(IV) in 80 ml of warm benzene was added 1.06×10^{-2} mol of the appropriate dithioacid in 30 ml of benzene. After refluxing for one hour, the initial greenish-brown solution had changed to either a dark blue solution (Mo(fdtb)$_4$ and Mo(acdtb)$_4$) or a greenish-black solution (Mo(dtnap)$_4$). The refluxing was discontinued and the solution filtered while hot. The benzene was then removed on a rotary evaporator. The complex was recrystallized twice from chloroform/ethanol. The crystals were dried under vacuum at 78°C for eight hours. *Yield:* Mo(fdtb)$_4$, 1.52 g (73.4%); Mo(acdtb)$_4$, 2.35 g (80.1%); Mo(dtnap)$_4$, 1.86 g (76.9%).

Preparation of Mo(fordtb)$_4$ and Mo(bendtb)$_4$

1.00 g (2.66×10^{-3} mol) of tetrachlorobis(butyronitrile)molybdenum(IV) in 80 ml of warm benzene was added to 1.06×10^{-2} mol of the appropriate dithioacid in 25 ml of benzene. fordtbH, being insoluble in benzene, was reacted as a suspension. After an hour of refluxing, the initial greenish-brown solution had changed to dark blue-green. The heating was discontinued and the solution then filtered while hot. No solvent nor solvent mixtures could be found that would effectively separate the impurities from the complexes through recrystallization. The separation was therefore accomplished by column chromatography using silica gel with benzene as the elutant. A glass column (diameter 2.5 cm) was packed to a depth of 15 cm with silica gel (as a benzene slurry). A constant pressure of 8 lbs/psi of nitrogen was maintained on the top of the column. The complexes eluted as slow moving broad blue bands preceded by pink, yellow, and green bands eluting in that order. Mo(bendtb)$_4$ could then be recrystallized from benzene/ethanol. No suitable solvent nor solvent system was found for recrystallization of Mo(fordtb)$_4$. It was obtained as a blue solid upon removal of the benzene. The complexes were dried under vacuum at 78°C for 8 hours.

Yield: Mo(fordtb)$_4$, 1.56 g (74.3%); Mo(bendtb)$_4$, 2.14 g (71.4%).

Preparation of Mo(cdtb)$_4$

2.01 g (1.06 x 10^{-2} mol) of 4-chlorodithiobenzoic acid in 30 ml of benzene were added to 1.00 g (2.66 x 10^{-3} mol) of tetrachlorobis(butyronitrile)molybdenum(IV) in 80 ml of warm benzene. After forty-five minutes of refluxing, the solution was green. The complex was purified on an alumina column using benzene as the elutant. A yellow band stayed at the top of the column while a large blue band (the complex) traveled down the column. The complex was then recrystallized from benzene. The crystals were dried under vacuum for eight hours at 78°C. *Yield:* 1.50 g (66.7%).

Preparation of Mo(dtmes)$_4$

To 2.09 g (1.06 x 10^{-2} mol) of dithiomesitoic acid in 30 ml of benzene was added 1.00 g (2.66 x 10^{-3} mol) of tetrachlorobis(butyronitrile)molybdenum(IV) in 80 ml of warm benzene. An immediate precipitation of a dark green powder occurred. The benzene was heated to reflux for one hour, after which the mixture was filtered while hot. The dark green precipitate was washed with 40 ml of hot benzene and then with 100 ml of hot chloroform. The precipitate was dried under vacuum at 78°C for eight hours. It is very slightly soluble in benzene and chloroform and insoluble in ether, alcohol, and sat. hydrocarbons. *Yield:* 1.62 g (69.5%).

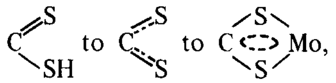
Preparation of Mo(badtb)$_4$

To 1.00 g (2.66 x 10^{-3} mol) of tetrachlorobis(butyronitrile)molybdenum(IV) in 80 ml of warm benzene were added 2.99 g (1.06 x 10^{-2} mol) of *p*-dibutylaminodithiobenzoic acid in 25 ml of benzene. A dark green precipitate formed immediately. The mixture was refluxed for one hour and then cooled to room temperature. The green to violet precipitate was collected by filtration, washed with 40 ml of benzene, and dried under vacuum. To neutralize any hydrochloride salt that may have formed, the dried precipitate was stirred with 100 ml of 3*M* NaOH solution for two minutes. It was then collected and washed several times with 50 ml of water. After being dried under vacuum, the dark green powder was recrystallized from benzene. The crystals were dried under vacuum at 78°C for 8 hours. *Yield:* 2.5 g (77.3%).

RESULTS AND DISCUSSION

In Table I are listed the 13 deeply colored molybdenum(IV) complexes and the corresponding tetraalkylammonium salts of the ligands prepared in this study, their colors, melting (or decomposition) temperatures and their elemental analyses. Perhaps the only thing noteworthy about the decomposition points of the complexes is that those which have electron-withdrawing groups *para* to the CS_2 group exhibit generally lower values than those which have electron-donating groups *para* (or *ortho*) to the CS_2 group. The complex with both *ortho* and *para* donating groups, Mo(dtmes)$_4$, is markedly more stable (by some 70–100 degrees) than any other complex.

In Table II are listed some of the more pertinent and characteristic infrared bands of the complexes. Our band assignments agree with those made previously[2] and generally there is nothing unexpected or unusual in the data. In Table III are some additional IR data which do exhibit some interesting trends. Consider the shifts in the carbonyl absorptions. First there is the expected frequency decrease in the *para*-substituted carbonyl as it changes from CH_3CO- to C_6H_5CO-, of 25–30 cm^{-1}, in acid, salt and complex. Then there is the observed frequency increase from acid to salt and a further increase from salt to molybdenum complex. This increase is probably caused by successively increasing charge delocalization from the phenyl ring to the dithiocarboxylate group. This effect, which increases from



is probably a combination of resonance and inductive effects which strengthens, via the pi electron system, the C=O pi bond.

The data for the *para*-fluoro derivatives shows a 30 cm^{-1} decrease in the phenyl-fluorine frequency from acid to salt but a nearly comparable increase from salt to complex. This behavior cannot be explained in the same way as was the carbonyl data since it has been shown[7] that as the X groups in substituted fluorobenzenes become more electronegative, the C–F stretchings frequency increases. On the other hand, this behavior can be explained by the carbon-13 nmr data for the fluorine compounds, to be presented in a forthcoming paper. That data suggests that the carbon attached to the fluorine has approximately the same electron density in both the

TABLE I
Molybdenum(IV) complexes and tetraalkylammonium salts prepared in this study

Compound	Color	m.p. C°[a]	C		H		N	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
Mo(*p*-dtt)$_4$ [b]	dark blue needles	260° (d)	50.24	50.31	3.70	3.71		
Mo(acdtb)$_4$ [c]	dark blue plates	235° (d)	49.30	49.57	3.22	3.29		
Mo(dtb)$_4$	dark blue	241° (d)	47.44	47.01	2.85	2.77		
Mo(*o*-dtt)$_4$	dark blue-violet needles	249° (d)	50.24	50.70	3.70	3.85		
Mo(mdtb)$_4$	dark green prisms	238° (d)	46.36	46.62	3.41	3.53		
Mo(phdtb)$_4$	dark green needles	245° (d)	61.63	61.59	3.59	3.85		
Mo(fdtb)$_4$	dark blue-violet plates	264° (d)	43.07	43.18	2.07	2.14		
Mo(cdtb)$_4$	dark blue needles	260° (d)	39.72	40.66	1.91	1.91		
Mo(fordtb)$_4$	dark blue powder	236° (d)	46.81	46.59	2.46	2.63		
Mo(bendtb)$_4$	dark blue needles	241° (d)	59.77	59.43	3.23	3.18		
Mo(dtnap)$_4$	greenish-black plates	251° (d)	58.13	57.63	3.11	3.09		
Mo(dtmes)$_4$	dark green powder	343° (d)	54.76	54.12	5.07	4.88		
Mo(badtb)$_4$	emerald green feathers	277° (d)	59.17	59.37	7.30	7.25	4.60	4.46
TEAdtb	dark brown prisms	137–138	63.54	63.76	8.91	8.98	4.94	4.91
TEA*p*-dtt	maroon needles	114–115	64.58	64.03	9.16	9.17	4.71	4.58
TEAmdtb	brown plates	110–111	61.28	61.38	8.70	8.84	4.47	4.39
TEAfdtb	dark maroon needles	87–88	59.75	59.62	8.04	8.28	4.65	4.56
TEAacdtb	dark brown rectangles	64–65	62.71	63.06	8.38	8.83	4.30	4.21
TPAcdtb	maroon microcrystals	83–84	61.00	61.21	8.64	8.25	3.75	3.75
TPAphdtb	dark brown needles	139–140	72.22	72.81	8.99	9.39	3.37	3.22
TPAfydtb	brown plates	82–83	65.33	65.25	9.07	9.43	3.81	3.72
TPAbendtb	mauve plates	117–119	70.37	70.17	8.42	8.65	3.16	3.02
TPAbadtb	brown plates	102–103	69.45	69.41	10.82	9.91	6.00	5.97
TPA*o*-dtt	red plates	131–132	67.91	68.30	9.99	9.87	3.96	3.93
TPAdtmes	orange plates	145–146	69.21	69.41	10.32	9.77	3.67	3.57
TPAdtnap	red-orange needles	130–131	70.88	71.01	9.07	9.39	3.59	3.44

[a] d indicates decomposition at the indicated temperature.

[b] Other analyses – Calcd: Mo, 12.54; S, 33.53. Found: Mo, 12.57; S, 32.52.

[c] Other analyses – Calcd: Mo, 10.94; S, 29.24. Found: Mo, 10.84; S, 29.46.

TABLE II
Pertinent IR bands of the molybdenum complexes in cm^{-1}

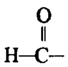
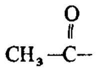
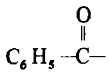
	$\bar{\nu}_{\text{phenyl-C}}$	$\bar{\nu}_{\text{asyCSS}}$	$\bar{\nu}_{\text{syCSS}}$	$\bar{\nu}_{\text{Mo-S}}$	$\bar{\nu}_{\text{C=O}}$
Mo(dtb)$_4$	1270 vs	1020 vs	950 m	340 w	
Mo(f-dtt)$_4$	1275 vs 1260 s	1035 vs 1020 m	952 s	340 w	
Mo(*o*-dtt)$_4$	1250 m	1020 vs	950 m 945 m	335 w	
Mo(mdtb)$_4$	(1280) 1268 vs	1030 s	950 s	335 w	
Mo(cdtb)$_4$	1272 s 1255 m	1030 s	950 s	335 w	
Mo(fdtb)	1275 vs 1260 vs	1025 s	954 m	330 w	
Mo(phdtb)$_4$	1274 s	1030 vs	955 m	320 w	
Mo(fordtb)$_4$	1260 mw	1032 m	950 mw	330 w	1695 vs
Mo(acdtb)$_4$	1265 vs (br) (1255)	1035 m	950 m	330 w	1685 vs
Mo(bendtb)$_4$	1275 vs (br)	1032 s	938 s 920 s	335 w	1660 vs
Mo(dtmes)$_4$	1250 vw	1035 m	962 m	330 w	
Mo(badtb)$_4$	1290 vs	1015 mw	950 mw	335 w	
Mo(dtnap)$_4$	1235 s (br)	1005 m	930 mw	345 w	

Values in parentheses are shoulders.

s = strong; m = medium; w = weak; v = very; br = broad.

acid and molybdenum complex, whereas in the anion that carbon has a slightly greater electron density. This is in agreement with the observed decrease and then increase in IR stretching frequency on going from acid to salt to complex.

TABLE III
Selected IR frequencies of four acids, their salts and Mo complexes

R in the p-R-$C_6H_4CS_2$ ligand	Acid	$\bar{\nu}_{\text{C=O}}$ salt	Mo complex
 $H-\overset{\overset{O}{\|}}{C}-$	(a)	1683 vs	1695 vs
 $CH_3-\overset{\overset{O}{\|}}{C}-$	1670 s	1681 vs	1685 vs
 $C_6H_5-\overset{\overset{O}{\|}}{C}-$	1645 vs	1650 vs	1660 s
F (b)	1240 vs	1210 vs	1235 vs

[a] Very weak or missing, shifted to lower frequency due to hydrogen bonding in this hydrated acid.

[b] Values are for $\bar{\nu}$ phenyl-F.

Data for the electronic spectra of the thirteen molybdenum dithiocarboxylato complexes are listed in Table IV. The absorption data for the free acids and their anions are listed for comparison.

Our data and spectral interpretations are in agreement with those of Piovesana and Sestili[2] and with the more recent work of Nieuwpoort and Steggerda.[8,9] In the latter study, spectral assignments were made for a number of Mo(IV) and Mo(V) tetrakisdithiocarbamato complexes along with two Mo(IV) tetrakisdithiocarboxylato complexes, Mo(*p*-dtt)$_4$ and Mo(dtnaf)$_4$ (naf = 2-naphthoyl). With the aid of extended Hückel M.O. calculations, they have divided the spectra of the dithiocarboxylato complexes into three classifications.

a) The high intensity absorptions around 30 kK were attributed to internal ligand π-π^* transitions. These have previously been observed to be above 28 kK.[10-12]

b) The absorptions between 11 and 29 kK were assigned to charge transfer transitions.

c) d-d transitions were attributed to absorptions occurring between 7 and 11 kK.

TABLE IV
Visible–ultraviolet bands, in kK units, and their intensities for Mo(IV) complexes, the acid ligands and their tetraalkylammonium salts[a,b]

Mo(dtb)$_4$	13.0 sh[c]	17.3(3.84), 20.5(3.68), 21.7(3.64)	31.3(4.96), 33.9(4.79)
dtbH		19.4(2.00)[d]	29.9 sh, 33.0(4.11)
TEAdtb		19.8(2.23)[d]	27.0(3.90), 35.3(4.01)
Mo(*p*-dtt)$_4$	12.8 sh[c]	17.1(3.98), 20.8(3.80), 21.7(3.79)	29.4(4.73), 32.8(4.75)
p-dttH		19.2(2.40)[d]	29.4 sh, 31.7(4.65)
TEA*p*-dtt		19.3(2.19)[d]	26.8(3.85), 32.8(4.04)
Mo(*o*-dtt)$_4$	12.0(4.01), 13.5 sh	18.0(3.71), 20.4(3.67), 22.2 sh	30.8 sh, 33.8(4.75)
o-dttH		19.8(2.03)[d]	32.7(3.97)
TEA*o*-dtt		20.1(2.11)[d]	28.4(4.17)
Mo(mdtb)$_4$	12.9 sh[c]	16.9(3.89), 21.3(3.74), 22.5(3.76)	27.4(4.86), 30.8(4.75)
mdtbH		19.4(2.48)[d]	29.1(4.26), 29.9(4.19)
TEAmdtb		19.4(2.29)[d]	27.0(3.92), 30.8(4.14)
Mo(cdtb)$_4$	12.7 sh[c]	17.1(4.04), 20.4(3.88), 21.7 sh	29.7(4.78), 32.9(4.81)
cdtbH		19.0(2.05)[d]	29.4 sh, 32.3(4.24)
TEAcdtb		19.2(2.26)[d]	26.7(3.84), 34.5(4.05)
Mo(fdtb)$_4$	12.9 sh[c]	17.4(3.69), 20.7(3.52), 21.7(3.51)	30.6(4.75), 33.7(4.76)
fdtbH		19.2(2.00)[d]	30.8(3.94), 32.8(4.16)
TEAfdtb		19.2(2.08)[d]	26.8(3.89), 34.2(3.98)
Mo(phdtb)$_4$	12.9 sh[c]	16.6(3.92), 20.4 sh, 21.5 sh	27.0(4.96), 29.7(4.98)
phdtbH		19.0(2.16)[d]	29.2(4.26)
TPAphdtb		19.2(2.58)[d]	27.0(3.97), 31.8(4.38)
Mo(fordtb)$_4$	12.8 sh[c]	16.4(3.90), 19.6(3.74), 20.8 sh	30.0(4.92), 32.5 sh
fordtbH		18.7(2.12)[d]	28.8 sh, 33.4(4.26)
TPAfordtb		19.1(2.58)[d]	27.8(3.69), 33.9(4.24)
Mo(acdtb)$_4$	12.9 sh[c]	16.5(3.98), 19.8(3.82), 20.9 sh	30.3(4.90), 32.3 sh
acdtbH		18.8(2.15)[d]	29.4 sh, 33.3(4.27)
TEAdtb		19.6(2.66)[d]	26.5(3.71), 34.2(4.21)
Mo(bendtb)$_4$	12.7 sh[c]	16.5(4.01), 19.8(3.82), 21.1 sh	29.7(4.99), 32.3(4.97)
bendtbH		18.8(2.12)[d]	29.6 sh, 33.3(4.31)
TPAbendtb		19.2(2.74)[d]	27.4(3.81), 33.7(4.29)
Mo(dtmes)$_4$	12.9(3.61), 14.1 sh	17.4 sh, 21.7(3.59), 23.2 sh	32.3 sh, >43.5
dtmesH		19.8(1.90)[d]	32.9(4.03)
TPAdtmes		20.2(1.92)[d]	28.4(4.20)
Mo(badtb)$_4$	<11.8	15.9(4.21), 17.9 sh, 21.4(5.05)	24.4(4.68), 26.9 sh
badtbH		19.4(2.84)[d]	25.8(4.53)
TPAbadtb		19.4(2.84)[d]	25.8(4.53)
Mo(dtnap)$_4$	11.9(4.07), 13.3 sh	17.9(3.73), 20.4(3.76)	25.3(4.42), 27.3(4.56), 40.0(4.81)
dtnapH		19.6(2.20)[d]	28.0(3.60), 33.1(4.80)
TPAdtnap		20.0(2.26)[d]	28.2(4.16), 30.3 sh

[a] TEA = Tetraethylammonium cation; TPA = Tetrapropylammonium cation.

[b] sh = shoulder; log ϵ in parentheses.

[c] Shoulder of an intense charge transfer band which may overlap a d-d transition. Not measured below 11.8 kK where maxima is expected to occur.

[d] n → π band of thiocarbonyl group.

In support of the foregoing assignments, we have found no absorptions in the 7–18 kK region for several Ti(IV) and Sn(IV) dithiocarboxylato complexes also prepared by us.[13]

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