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Dioxomolybdenum(VI) Complexes of Methylpiperidine Dithiocarbamates

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Three new complexes of dioxomolybdenum(VI) of the general formula $[MoO_2(Rdtc)_2]$, where $Rdtc^-$ refer to 2-, 3- or 4-methylpiperidine (2-, 3-, 4-Mepipdtc) dithiocarbamates, have been prepared. The complexes have been characterized by elemental analysis, conductometric measurements, electronic, IR and NMR spectroscopy. Through contributions of resonance structures which lead to an effective dianion electronic structure the two dithiocarbamate ions join with both the sulphurs to the molybdenum atom. The complexes contain a *cis*-MoO_2 group and are of octahedral geometry. The position of the methyl group on the piperidine ring has influence on the $\nu(C\overset{\cdots}{-}N)$ and $\nu(C\overset{\cdots}{-}S)$ vibrations which decrease in the order 2-Mepipdtc > 3-Mepipdtc > 4-Mepipdtc.

Key Words: Dithiocarbamates, Molybdenum(VI) complexes, MoO_2^{2+} group.

INTRODUCTION

Molybdenum complexes with organic ligands are the compounds of great theoretical and practical interest, especially valuable as model systems for biochemical processes. However, such attempts enrich the coordination chemistry of molybdenum in its higher oxidation state. The presence of $[Mo(VI)O_2]^{2+}$ group is of importance in fully oxidized states of a number of redox enzymes taking part in the biological fixation of nitrogen[1]. Relevance of molybdenum-sulphur bond to these and related assemblies makes their investigations more significant[1–3]. On the other hand, the dithiocarbamate (*Rdtc*$^-$) ligands are known to be strong and form stable complexes with many transition metals[4–7]. Interest in dithiocarbamate complexes arises because of both their varied structures depending on mono- or bidentate ligands function and of their biological activity[8, 9]. Besides, these coordination compounds have intriguing properties arising from good corrosion inhibitors in acidic media[10, 11].

We embarked on the present study to synthesize dioxomolybdenum(VI) complexes with 2-, 3-, or 4-Mepipdtc dithiocarbamato ligands. As a contribution

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to the problem of a coordinating behaviour of the heterocyclic dithiocarbamates, their mode of coordination was determined, and particularly the spectrochemical properties of these compounds were discussed. In order to get further insight into the electronic structure of the complexes, an effort has been focused on the methyl substituent in the piperidine ring on the C$\overset{...}{-}$N and C$\overset{...}{-}$S bonds and on the electronic structure of the complexes. Furthermore, the ability to influence the bond order seems to be related closely to the electronic properties of the *Rdtc*$^-$ ligand as a whole, not just the sulphur atoms bonded to the molybdenum atom. The position of the substituent can also influence the behaviour of the *Rdtc*$^-$ ligands through variation in the electronic releasing ability of the different amines.

EXPERIMENTAL

All chemicals used were commercial products of analytical reagent grade. The sodium salts of *Rdtc*$^-$ and $MoO_2(acac)_2$ were obtained according to the procedure described in the literature[6, 12].

To a methanolic solution (5 mL) of $MoO_2(acac)_2$ (330 mg, 1 mmol) was added 2 mmol of dithiocarbamate (*i.e.*, 466 mg of 2-, 3- or 4-MepipdtcNa·$2H_2O$) dissolved in water (5 mL) dropwise during 1 h with stirring and heating on a water bath at 40°C. The mixture was then continuously stirred under reflux for about 2 h. The filtrate was concentrated in a vacuum evaporator to 10 mL. Upon cooling the mixture in a refrigerator two days later crude products were precipitated. After recrystallization from hepten : toluene mixture (1 : 1, v/v) light brown crystalline substances of the corresponding complexes were filtered. Analytical results confirmed the composition proposed.

(1) $[MoO_2(2\text{-Mepipdtc})_2]$ Yield: 106 mg (17%). Anal. Calcd. for $C_{14}H_{24}MoN_2O_2S_4$ (476.36) (%): C, 35.26; H, 5.08; N, 5.88; Mo (mg/dm^{-3}), 19.60. Found: C, 35.65; H, 4.69; N, 5.91; Mo, 19.20.

(2) $[MoO_2(3\text{-Mepipdtc})_2]$ Yield: 61 mg (10%). Anal. Calcd. for $C_{14}H_{24}MoN_2O_2S_4$ (476.36) (%): C, 35.26; H, 5.08; N, 5.88; Mo (mg/dm^{-3}), 19.60. Found: C, 35.23; H, 5.22; N, 5.41; Mo, 19.80.

(3) $[MoO_2(4\text{-Mepipdtc}_2]$ Yield: 59 mg (10%). Anal. Calcd. for $C_{14}H_{24}MoN_2O_2S_4$ (476.36) (%): C, 35.26; H, 5.08; N, 5.88; Mo (mg/dm^{-3}), 19.60. Found: C, 35.72; H, 4.89; N, 5.99; Mo, 20.05.

Molar conductivity of methanolic solutions (1×10^{-3} mol dm^{-3}) was measured at 20°C by a Jenway-4009 conductometer. Electronic spectra of methanolic solutions (1×10^{-3} M) were recorded on a GBC UV/VIS 911A spectrophotometer. IR spectra in the 4000–400 cm^{-1} range were measured on a Perkin-Elmer 317 25x FTIR spectrophotometer, using KBr discs. ^{1}H and ^{13}C NMR were run with a Gemini YH 200 spectrometer in DMSO-d_6 at room temperature. The chemical shifts were determined relative to TMS.

RESULTS AND DISCUSSION

The complexes were obtained by mixing the reactants in a 1 : 2 mole ratio in a substitution reaction of the two acetylacetonato anions in $[MoO_2(acac)_2]$ complex by the *Rdtc*$^-$ ligands.

$$[MoO_2(acac)_2] + 2RdtcNa\cdot 2H_2O \rightarrow [MoO_2(Rdtc)_2] + 2acacNa + 2H_2O$$

The new complexes appear to be light brown microcrystalline substances, stable under atmospheric conditions and soluble in methanol, ethanol, heptane, toluene and dimethylsulfoxide, insoluble in water, chloroform, dichlormethane and benzene. The non-electrolyte nature of the obtained complexes was confirmed by the low molar conductivities[13] (λ_M = 25.57; 24.50 and 16.30 $\Omega^{-1}cm^2\ mol^{-1}$ for **(1)**–**(3)** complexes, respectively).

The complexes are diamagnetic as expected for the $4d^0$ configuration. Since there are no d electrons, the splitting from d-d transitions is not discernible. The absorptions appearing in the electronic spectra in the range 280–400 nm arise from charge transfer and intraligand transitions, especially due to the NCS_2 chromophore[14], but the assignments of charge-transfer spectra have been a controversial area[15, 16].

In Table-1 the pertinent IR data, *i.e.*, $\nu(C\overset{\cdots}{-}N)$, $\nu(C\overset{\cdots}{-}S)$ vibrations of the free and coordinated *Rdtc*$^-$ ligands, ν(Mo—S) bands, as well as the MoO_2^{2+} core vibrations of the complexes **(1)**–**(3)** are collected.

TABLE-1

IMPORTANT IR BANDS (cm^{-1}) FOR THE COMPLEXES (1)–(3)

Compound	ν_{sym}(Mo=O)	ν_{asym}(Mo=O)	ν(C—N)	ν(C—S)	ν(M—S)
Complex (1)	863 m	838 s	1398 s	951 s	425 w
Complex (2)	881 m	849 s	1408 s	953 s	431 m
Complex (3)	892 v	840 s	1412 s	966 s	439 m
2-MepipdtcNa	—	—	1407 vs	943 s	—
3-MepipdtcNa	—	—	1418 vs	951 s	—
4-MepipdtcNa	—	—	1424 vs	950 s	—

Concerning the electronic and structural characteristics of described compounds, there are several regions in the IR spectra of considerable interest. Symmetric and antisymmetric stretching vibrations observed near 900 cm^{-1} can be attributed to a *cis*-$[MoO_2]^{2+}$ core[17]. Generally, the ν_{sym}(Mo=O) are higher in wave numbers than the ν_{asym}(Mo=O)[18]. The 1430–1390 cm^{-1} region is associated primarily with the thioureide vibration and is attributed to the $\nu(C\overset{\cdots}{-}N)$ vibrations of the S_2C—NR_2 bond [4–7] (Table-1). An increase in the double bond character of the $C\overset{\cdots}{-}N$ bond results in higher frequency for these vibrations. This fact can be ascribed to the electron releasing ability of the heterocyclic group which forces high electron density towards the sulphur atoms, *via* the π system, thus producing greater double bond character in the $C\overset{\cdots}{-}N$ bond. All the complexes show $\nu(C\overset{\cdots}{-}N)$ bands in the 1430–1390 cm^{-1} range, which lie between ν(C=N) and ν(C—N), in the 1690–1640 and 1350–1250 cm^{-1} range, respectively.

A region between 1100–950 cm^{-1} is associated with the ν(CSS) vibrations and has been effectively used in differentiating between monodentate and bidentate *Rdtc*$^-$ ligands[4–7, 19]. The presence of only one strong band supports bidentate coordination of the dithio ligands, whereas a doublet is expected in the case of monodentate coordination[4, 19]. Further confirmation of such behaviour gives the position of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ vibrations; in fact this band undergoes blue shifts in these complexes, while for unidentate coordination this stretching would be shifted towards lower wave numbers or remains unchanged in comparison to the value of free dithiocarbamate sodium salts[4]. New absorption bands in the 440–420 cm^{-1} region, absent in the spectra of the free *Rdtc*$^-$ ligands, are in good agreement with available literature data[19] and may be associated with ν(Mo—S) vibrations.

The position of the methyl group in the piperidine ring influences the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ values, which are decreased in the order 2-Mepipdtc > 3-Mepipdtc > 4-Mepipdtc. This fact could be explained by taking into account the electron releasing ability of the heterocyclic ring bearing a methyl substituent which, as discussed above, forces the electron density towards the sulphur atoms. It might be because of the rigid heterocyclic ring system due to the high symmetry of the 4-Mepipdtc ligand with the methyl group in *para* position, a tendency to release electrons to the carbon-nitrogen bond (in complex 3) is the least[6].

The methyl group absorptions, both in the free ligands and in the complexes, as medium bands in the 2970–2960 cm^{-1} range can be related to the asymmetric CH_3 stretching vibration, while the bands at 1385–1360 cm^{-1} and 1210–1170 cm^{-1} are due to the degenerate symmetric and rocking vibrations of the methyl group, respectively.

The medium band presented at 529 cm^{-1} can be attributed to the ν(CS) + δ(SCS) and to a four membered chelate ring deformation contribution[20].

As regards the ^{1}H NMR data (Table-2), there is proton signal as a triplet of the methyl group which, depends mainly on the symmetry shifts, moves downfield to 1.15, 0.86 and 0.91 ppm for complexes (1)–(3), respectively, relative to the corresponding free *Rdtc*$^-$ ligands (peaks at 1.20, 0.90 and 0.95 ppm). The other carbon protons depend on the position of the methyl group. The protons attached to carbon atoms C1-C3 for complexes (1)–(3) are rendered non-equivalent due to the position of the methyl group on the piperidine ring and coupling can occur between these sets of protons, giving rise to second-order effects and resulting in a more complicated spectrum in the region of δ 3.50–2.40 ppm.

TABLE-2

^{1}H NMR CHEMICAL SHIFTS* (IN ppm) FOR THE COMPLEXES (1)–(3)

Complexes	δ (ppm)
(1)	1.49, t, 1H (C1); 1.66, m, 2H (C2); 2.68, t, 2H (C3); 2.84, m, 2H (C4); 3.12, d, 2H (C5); 1.15, t, 3H (C6)
(2)	2.49, m, 2H (C1); 1.93, t, 1H (C2); 2.28, m, 2H (C3); 1.71, s, 2H (C4); 2.81, t, 2H (C5); 0.86, t, 3H (C6)
(3)	2.83, d, 2H (C1); 1.28, d, 2H (C2); 1.58, d, 1H (C3); 1.71, d, 2H (C4); 3.24, d, 2H (C5); 0.91, t, 3H (C6)

*In ppm relative to TMS. For the assignment of the various atoms see Fig. 1.

The various types of carbons have been successfully assigned (Table-3) and notations of these resonances are according to Fig. 1. There are six lines, which belong to the *Rdtc*$^-$ ligands, depending on the chemically equivalent nuclei. The last resonance, C6, is due to the methyl carbon for the complexes (1)–(3).

TABLE-3

^{13}C NMR CHEMICAL SHIFTS* (IN ppm) FOR THE COMPLEXS (1)–(3)

Complexes	δ (ppm)		
(1)	S_2CN	212.29	C1, 20.94; C2, 23.41; C3, 32.24; C4, 45.19; C5, 52.09; C6, 15.32
(2)	S_2CN	212.64	C1, 50.19; C2, 33.40; C3, 31.25; C4, 25.43; C5, 57.08; C6, 19.44
(3)	S_2CN	211.62	C1, 49.97; C2, 28.78; C3, 34.26; C4, 31.03; C5, 51.59; C6, 21.91

*In ppm relative to TMS. For the assignment of the various atoms see Fig. 1.

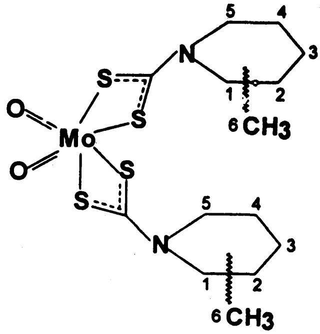

Fig. 1. Suggested Structures of the Complexes: 2-Mepipdtc (1), 3-Mepipdtc (2), 4-Mepipdtc (3).

A single signal is observed corresponding to the CS_2 moieties of *Rdtc*$^-$ in each complex, which indicates that the chemical environments of CS_2 moieties of two *Rdtc*$^-$ ligands bound to a *cis*-MoO_2 centre are equivalent to each other[21]. The chemical shifts of the CS_2 cores of *Rdtc*$^-$ are sensitive to the position of the substituent on the piperidine ring. The behaviour reflects the fact that the complex (3) due to its high symmetry with methyl substituent in *para* position exhibits the CS_2 signal at lower frequency.

The important feature of the IR spectra provides a consistent picture that the *Rdtc*$^-$ ligands are bound through both the sulphur atom as well as the molydbenum atom, as can be seen from the chemical environments of CS_2 moieties in NMR spectra. This bidentate S,S′ structure is again the most favourable. The geometry of the MoO_2S_4 core is an octahedron (Fig. 1) with the two terminal oxo ligands lying invariably in a *cis* position to each other, common for dioxomolybdenum(VI) complexes[21]. Unfortunately, single crystals of these complexes could not be obtained and as already indicated, IR spectra together with NMR spectral data confirm their most probable structures.

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