Structural study of molybdenum(VI) complexes containing bidentate ligands: Synthesis, characterization and DFT calculations

Raúl Colorado-Peralta, Mario Sanchez-Vazquez, Irán F. Hernández-Ahuactzi, Sonia A. Sánchez-Ruiz, Rosalinda Contreras, Angelina Flores-Parra, Silvia E. Castillo-Blum

Departamento de Química Inorgánica, Facultad de Química, Universidad Nacional Autónoma de México, C.P. 04510, México D.F., Mexico
Centro de Investigación en Materiales Avanzados, S.C. Alianza Norte 202, PIIT, Carretera Monterrey-Aeropuerto Km. 10, C.P. 66600, Apodaca N.L., Mexico
Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, C.P. 07360, México D.F., Mexico

ABSTRACT

A series of molybdenum(VI) complexes containing bidentate ligands: toluene-3,4-dithiol (1), 2-mercapto-phenol (2), 2-aminothiophenol (3), ethane-1,2-dithiol (4), dithiooxamide (5) and 2-thiopheno-carboxamide (6) are reported. The hexacoordinated molybdenum tris-chelates compounds: tris-(toluene-3, 4-dithiolate)molybdenum(VI) (7), tris-(2-mercapto-phenolate)molybdenum(VI) (8), tris-(2-aminothiophenolate)molybdenum(VI) (9), tris-(ethane-1,2-dithiolate)molybdenum(VI) (10), and the bis-chelates, which also contain coordinated oxo ligands: bis-(dithiooxamide)dioxomolybdenum(VI) (11) and bis-(2-thiopheno-carboxamide)dioxomolybdenum(VI) (12), were characterized by 1H and 13C NMR and IR spectroscopies, as well as elemental analyses and mass spectrometry. The structures of minimum energy of the coordination compounds were calculated using DFT (B3LYP/def2-TZVPP). Solid state structures of analogous compounds, as well as calculations indicated that the minimum energy structures correspond to those of trigonal prismatic geometry.

1. Introduction

Molybdenum has captured the interest of several research groups, since it has a rich chemistry, it occurs in various oxidation states, coordination numbers and geometries; it also plays an important role in biological processes [1]. Molybdenum is the only second row transition metal essential to life processes, from bacteria to humans. The pterin cofactor in molybdoenzymes contains molybdenum in a coordination state, coordination numbers and geometries; it also plays an important role in biological processes [1]. Molybdenum has been shown to be essential for many biological processes, including enzyme function, metabolic reactions, and DNA repair. The pterin cofactor in molybdoenzymes contains molybdenum in a coordination state, coordination numbers and geometries; it also plays an important role in biological processes [1]. Molybdenum has been shown to be essential for many biological processes, including enzyme function, metabolic reactions, and DNA repair.

Keywords:
Molybdenum complexes
Bidentate ligands
Trigonal prismatic
DFT calculations
Structural analysis

2. Experimental

2.1. Physical measurements

NMR spectra were obtained on a Varian VNMRS-400 [1H 399.78 MHz, 100.53 MHz 13C] and a Jeol GSX-Delta 270 MHz NMR spectra were obtained on a Varian VNMRS-400 [1H 399.78 MHz, 100.53 MHz 13C] and a Jeol GSX-Delta 270 MHz...
of tetrahydrofuran solution of bis-(acetylacetonate)dioxo-
bromomolybdenum(VI) (68 mg, 0.21 mmol). The reaction mixture was
stirred for 15 h at room temperature, filtered and the solvent evap-
orated. The solid was washed with pentane and dried in vacuum.

Scheme 2. Molybdenum coordination compounds with bidentate ligands.

[1H 270.17 MHz, 67.94 MHz 13C]. 1H and 13C spectra were acquired
using Si(CH3)4 as reference and tetrahydrofuran-d8 as solvent, in
5 mm diameter tubes. Melting points were measured in sealed
capillaries on a Mel-Temp Electrothermal Barnstead International
apparatus and are uncorrected. IR spectra were recorded on a Perkin-
Elmer FTIR/FTFIR Spectrum 400 spectrometer with a reflectance
ATR accessory. High-resolution mass spectra were obtained by
LC/MSD TOF on an Agilent Technologies instrument with ESI as
ionization source, using methanol as solvent (few drops of dimeth-
ylsulfoxide were added to accomplish the complete dissolution of
the solid in methanol). Elemental analyses were performed on a Perk-
inElmer Series II CHNS/O model 2400 analyzer. Cyclic voltam-
metry measurements were carried out at room temperature with a
three electrode cell using 0.1 M Bu4NPF6 as the supporting electro-
lite and all solutions were about 1 M.

2.3.2. Tris-(2-mercaptophenolate)molybdenum(VI): Mo(SOC6H4)3 (8)

Compound 8 was prepared by following the general procedure,
from 2-mercaptophenol (100 mg, 0.79 mmol) and bis-(acetylacet-
one)dioxomolybdenum(VI) (85 mg, 0.26 mmol). Compound 8 is a
viscous black liquid (0.11 g, 94 %). NMR (δ ppm, THF-
d8, 25 °C): 1H: 7.40 (d, 3H, H-6), 7.20 (J 8.2 Hz), 7.05 (dd, 3H, H-4, 8.2, 7.3 Hz), 6.75 (d,
3H, H-3), 8.11 Hz), 6.74 (dd, 3H, H-5, 8.2, 7.3 Hz). 13C: 155.6
(C-2), 129.5 (C-4), 128.4 (C-6), 120.0 (C-1), 119.8 (C-5), 115.0
(C-3). IR (ATR, v cm⁻¹): 1552, 1532, 1466, 1444 (C=C arom) 1179
(C-O), 746 (C–H or). CV (0.1 M Bu4NPF6, MeCN) E1/2 = -1.21,
-0.15 V. (–)TOF m/z (amu); Calc. for (C12H18MoO3S4): 456.9294.
S, 20.54. Found: C, 46.27; H, 2.70; S, 20.77.

2.3.3. Tris-(2-ami

2.3.4. Tris-(ethane-1,2-dithiolate)molybdenum(VI): Mo(S2C2H4)3 (9)

Compound 9 was prepared by following the general procedure,
from 1,2-ethanedithiol (100 mg, 1.06 mmol) and bis-(acetylacet-
one)dioxomolybdenum(VI) (87 mg, 0.27 mmol). Compound
9 is a dark green solid (0.12 g, 90 %). Mp > 400
°C. NMR (δ ppm, THF-
d8, 25 °C): 1H: 7.32 (d, 3H, H-6), 9.1 Hz), 6.99 (dd, 3H, H-4, 8.6, 8.5 Hz), 6.65 (d, 3H, H-3), 8.5 Hz), 6.57 (d, 3H, H-5, 8.1, 8.6 Hz), 4.48 (br s, 3H, H-3–H–H). 13C: 190.1. IR (ATR,
C–O), 724, 716 (C–H ortho). CV (0.1 M Bu4NPF6, MeCN) E1/2 = -1.28,
-0.14 V. (–)TOF m/z (amu); Calc. for (C12H18MoS4): 465.9409. Found:
S, 20.67. Found: C, 46.48; H, 2.53; N, 8.85; S, 20.69.

2.3.5. Bis-(dihioxamidate)dioxomolybdenum(VI): MoO(S2N2C2H4)2 (10)

Compound 10 was prepared by following the general proce-
dure, from 1,2-ethanedithiol (100 mg, 1.06 mmol) and bis-(acetylaceto-
one)dioxomolybdenum(VI) (115 mg, 0.35 mmol). Compound
10 is a black solid (0.12 g, 90 %). Mp > 400 °C. NMR (δ ppm, THF-
d8, 25 °C): 1H: 2.51 (br s, 12H, C–H).13C: 136.8 (C-5), 131.1
(C-2), 129.5 (C-4), 128.4 (C-6), 120.0 (C-1), 119.8 (C-5), 115.0
(C-3). IR (ATR, v cm⁻¹): 1585, 1512, 1440 (C
> C). NMR (δ ppm, THF-
d8, 25 °C): 1H: 9.39 (br s, 6H, N–H). 13C (ppm): 159.5 (C
 asym). CV (0.1 M Bu4NPF6, MeCN) E1/2 = -1.23, 0.49 V. Anal.
Calc. for C12H18MoN2S4: C, 19.35; H, 2.32; N, 5.16. Found: C, 19.52;
H, 3.59; N, 52.16.

2.3.6. Bis-(dithiooxamidate)dioxomolybdenum(VI): MoO(S2N2C2H4)2 (11)

Compound 11 was prepared by following the general proce-
dure, from dithiooxamidine (100 mg, 0.83 mmol) and bis-(acetylacet-
one)dioxomolybdenum(VI) (136 mg, 0.41 mmol). Compound
11 is a dark brown solid (0.14 g, 92 %). Mp > 400 °C. NMR (δ ppm, THF-
d8, 25 °C): 1H: 9.39 (br s, 6H, N–H). 13C (ppm): 190.1. IR (ATR,
C–O), 729, 716 (C–H prin). 3155, 1510 (C–S), 1261 (C–N), 933 (Mo–O sym), 904 (Mo–O asym). CV (0.1 M Bu4NPF6, MeCN) E1/2 = -1.52, 0.05 V. Anal. Calc. for C12H18MoN2S4: C, 13.11; H, 1.65; N, 15.29; S, 35.01. Found: C, 13.46; H, 1.48; N, 15.44; S, 35.08.
2.3.6. Bis-(2-thiophenecarboxamidate)dioxomolybdenum(VI): \( \text{MoO}_2(\text{S} \cdot \text{NOC}_5\text{H}_4)_2 \) (12)

Compound 12 was prepared by following the general procedure, from 2-thiophene-carboxamide (100 mg, 0.78 mmol) and bis-(acetylacetonate)dioxomolybdenum(VI) (128 mg, 0.39 mmol). Compound 12 is a green solid (0.14 g, 94%). Mp 154°C. NMR (\( \delta \) ppm, THF-\( d_8 \), 25°C). \(^1\)H: 7.58 (d, 2H, H-3, \( J \) 9.4 Hz), 7.55 (d, 2H, H-4, \( J \) 9.4 Hz), 7.04 (d, 2H, H-5, \( J \) 8.9 Hz), 6.82 (br s, 2H, N–H). \(^13\)C: 162.5 (C-1), 140.1 (C-2), 129.5 (C-4), 127.5 (C-3), 126.6 (C-5). IR (ATR, cm\(^{-1}\)): 3164 (N–H sec), 1600 (C=O), 1243 (C-N), 1652 (C=O), 934 (Mo=O sym), 903 (Mo=O asym). Anal. Calc. C\(_{10}\)H\(_8\)MoN\(_2\)O\(_4\)S\(_2\): C, 31.58; H, 2.12; N, 7.37; S, 16.86. Found: C, 31.71; H, 2.25; N, 7.13; S, 16.44%.

3. Computational details

Geometries to characterize all structures were optimized and harmonic vibrational frequencies were computed with the same level of theory using hybrid density functional theory (DFT-B3LYP) [50,51] in conjunction with the def2-TZVPP basis set, this level of theory considers the relativistic effects of molybdenum. All calculations are minimal true, since the values of the vibrational modes are all positive. These results were obtained with the GAUSSIAN 03 software package [52]. All structures were visualized by using the CHEMCRAFT v1.6 program [53].

4. Results and discussion

4.1. Synthesis of molybdenum(VI) compounds

Six molybdenum compounds were synthesized (7–12) from the reaction of bidentate ligands: toluene-3,4-dithiol (1), 2-mercaptophenol (2), 2-aminothiophenol (3), ethane-1,2-dithiol (4), dithiooxamide (5) and 2-thiophene-carboxamide (6), with bis-(acetylacetonate)dioxomolybdenum(VI) shown in Scheme 3. Five of these compounds are new, while 9 was previously reported, which was characterized only by X-ray diffraction crystal structure [25].

The ligands (1–6) were reacted with bis-(acetylacetonate)dioxomolybdenum(VI) in 3:1, 2:1 and 1:1 ligand to molybdenum molar ratios. Reactions were performed in THF using standard Schlenk techniques for anhydrous conditions, gradual changes in the color of the reaction solution were observed. Additional variations of reaction conditions were investigated, such as dropwise addition...
of ligand to metal, or metal to ligand; in all cases the reactions exclusively yielded trisubstituted (7–10) and disubstituted (11, 12) products, Scheme 4. These bidentate ligands form five-membered rings with molybdenum, favoring in most cases the formation of the tris-chelate complexes. All isolated solids are air stable. The reactions also yield H₂O and 2,4-pentadione, which are removed by vacuum evaporation. Maximum yield of the products occurs when the stoichiometry of the reactions is 3:1 for 7–10 and 2:1 for 11–12.

4.2. Spectroscopic studies

These new compounds are diamagnetic hexacoordinated (d₀), containing molybdenum(VI). ¹H and ¹³C chemical shifts were unequivocally assigned by 2D experiments HETCOR and COSY of the ligands and comparing with the spectra of the molybdenum compounds in the same solvent. ¹³C and ¹H NMR spectra of the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Selected δ (ppm, THF-d₈ at 25 °C) ¹³C and ¹H NMR for ligands 1–6 and molybdenum complexes 7–12. Proton NMR signals are displayed in italics.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>(1)</td>
<td>127.1</td>
</tr>
<tr>
<td></td>
<td>7.22</td>
</tr>
<tr>
<td>(7)</td>
<td>119.9</td>
</tr>
<tr>
<td></td>
<td>6.77</td>
</tr>
<tr>
<td>(2)</td>
<td>111.4</td>
</tr>
<tr>
<td></td>
<td>6.7 (d)</td>
</tr>
<tr>
<td>(3)</td>
<td>121.0</td>
</tr>
<tr>
<td></td>
<td>6.75 (d)</td>
</tr>
<tr>
<td>(11)</td>
<td>111.6</td>
</tr>
<tr>
<td></td>
<td>6.65</td>
</tr>
<tr>
<td>(4)</td>
<td>28.7</td>
</tr>
<tr>
<td>(10)</td>
<td>29.7</td>
</tr>
<tr>
<td>(5)</td>
<td>190.0</td>
</tr>
<tr>
<td>(6)</td>
<td>162.9</td>
</tr>
<tr>
<td></td>
<td>7.57</td>
</tr>
<tr>
<td>(12)</td>
<td>162.5</td>
</tr>
<tr>
<td></td>
<td>7.58</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Selected stretching vibrations (cm⁻¹) for ligands 1–6 and molybdenum complexes 7–12.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ν(S–H)</td>
</tr>
<tr>
<td>(1)</td>
<td>2552</td>
</tr>
<tr>
<td>(7)</td>
<td>2526</td>
</tr>
<tr>
<td>(2)</td>
<td>2522</td>
</tr>
<tr>
<td>(3)</td>
<td>2551</td>
</tr>
<tr>
<td>(4)</td>
<td>2522</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>2551</td>
</tr>
<tr>
<td>(10)</td>
<td>2522</td>
</tr>
<tr>
<td>(11)</td>
<td>2551</td>
</tr>
</tbody>
</table>

Fig. 1. Twist angles for trigonal prismatic vs. octahedral geometry.

Fig. 2. Superimposition of the structure of compound 9 reported by X-ray diffraction analyses (gray), with its modeled structure (black).
molybdenum complexes in tetrahydrofuran-$d_8$, at room temperature, show no significant changes in the chemical shift and coupling constants, as compared with those of the ligands, however the shape of the signals shows differences, especially in the proton spectra where they become wider and the multiplicity decreases. Compound 7 has a methyl substituent on the aromatic ring, while 8 and 9 contain [S,O] and [S,N] donor atoms respectively, therefore it would be possible to obtain several isomers of the compounds.

Table 3

<table>
<thead>
<tr>
<th></th>
<th>Mo(SNC$_6$H$_5$)$_3$ (reported)</th>
<th>Mo(SNC$_6$H$_5$)$_3$ (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond lengths</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(1)–N(1)</td>
<td>1.998(4)</td>
<td>2.034</td>
</tr>
<tr>
<td>Mo(1)–N(2)</td>
<td>2.005(4)</td>
<td>2.034</td>
</tr>
<tr>
<td>Mo(1)–N(3)</td>
<td>1.989(4)</td>
<td>2.034</td>
</tr>
<tr>
<td>Mo(1)–S(1)</td>
<td>2.412(1)</td>
<td>2.403</td>
</tr>
<tr>
<td>Mo(1)–S(2)</td>
<td>2.419(1)</td>
<td>2.403</td>
</tr>
<tr>
<td>Mo(1)–S(3)</td>
<td>2.424(1)</td>
<td>2.403</td>
</tr>
<tr>
<td>N(1)–C(6)</td>
<td>1.356(6)</td>
<td>1.360</td>
</tr>
<tr>
<td>N(2)–C(12)</td>
<td>1.371(6)</td>
<td>1.360</td>
</tr>
<tr>
<td>N(3)–C(18)</td>
<td>1.370(6)</td>
<td>1.360</td>
</tr>
<tr>
<td>S(1)–C(1)</td>
<td>1.709(6)</td>
<td>1.729</td>
</tr>
<tr>
<td>S(2)–C(7)</td>
<td>1.728(5)</td>
<td>1.729</td>
</tr>
<tr>
<td>S(3)–C(13)</td>
<td>1.735(5)</td>
<td>1.729</td>
</tr>
<tr>
<td><strong>Bond angles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)–Mo(1)–S(1)</td>
<td>78.06(11)</td>
<td>77.83</td>
</tr>
<tr>
<td>N(2)–Mo(1)–S(2)</td>
<td>77.28(12)</td>
<td>77.83</td>
</tr>
<tr>
<td>N(3)–Mo(1)–S(3)</td>
<td>78.13(12)</td>
<td>77.83</td>
</tr>
<tr>
<td><strong>Twist angles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(1)–C(1)–C(6)–N(1)</td>
<td>4.1</td>
<td>3.8</td>
</tr>
</tbody>
</table>

However, it can be concluded that only the most symmetric isomer of the compounds is present in solution, since there is only one signal per carbon atom of the ligands and one signal per proton of the ligands. It was also observed an effect of deprotection of C1 and C2, α to the Mo–X bond (X = S, O, N), Table 1.

Comparison of the IR (ATR) spectra of the ligands with those of the molybdenum complexes show the deprotonation of the SH, OH and NH groups upon coordination, confirming their bidentate nature. Spectra of molybdenum compounds show the characteristic vibrations assigned to the stretching bands such as $\nu$(C=C)arom (1440–1610 cm$^{-1}$), $\nu$(C–H)arom (810–740 cm$^{-1}$) for 7–9 compounds. Derivatives 8 and 9 show $\nu$(C–H)ortho disubstituted stretching at 746 and 752 cm$^{-1}$ respectively. Derivatives 11 and 12 show $\nu$(Mo=O) stretching symmetric and asymmetric vibrations at 933 and 904 cm$^{-1}$ (11), 934 and 903 cm$^{-1}$ (12), respectively. A significant change is observed in the $\nu$(N–H) stretching band of compounds 9, 11 and 12. The ligands 3, 5 and 6 show two bands characteristics of primary amines at 3426, 3352 cm$^{-1}$ (3), 3293, 3210 cm$^{-1}$ (4) and 3357, 3285 cm$^{-1}$ (5), while the products show a single band characteristic of secondary amines 3275 cm$^{-1}$ (9), 3135 cm$^{-1}$ (11) and 3164 cm$^{-1}$ (12), Table 2.

4.3. Structural analyses by DFT calculations

An important aim in our investigation was the structural analysis of the different complexes and the evaluation of how the different geometries and point groups were stabilized. The structures of minimum energy were determined by means of the frequency analyses, all stationary points are minimal true, since the values of the vibrational modes are all positive. The calculated results were compared with those from the IR and NMR spectroscopic
data of the herein synthesized compounds, which were in good agreement.

The crystal structures of analogous complexes containing molybdenum in different oxidation states and bidentate sulfur ligands have been reported in the Cambridge Structural Database [20–40] as well as the active site of molybdenum proteins, reported in the Protein Data Bank [3,10,13,16,18], it has been observed that these compounds stabilize trigonal prismatic geometry. The preference of this geometry has been explained in terms of the efficient stabilization of the molecular orbitals of...
molybdenum complexes, despite the increase in the electronic repulsion of the ligands [twist angles (δ): trigonal prism 0°, octahedron 60°], [38–44] Fig 1.

Validation of the calculations results when the calculated (black) and crystal reported (gray) [25], structures of 9 are superimposed, Fig 2. The differences between the bond lengths and angles for its reported and calculated structures, are shown in Table 3, the similarity of the values indicates that the difference between them are negligible.

Analysis of all possible geometries of the molybdenum compounds 7–12 by changing the orientation of the bidentate ligands to find the global minimum resulted in various symmetries: C1/C1, C3 and C3v for 7–9, C3 for 10, C1/C1 and C2 for 11 and 12. C3 happened to be the most stable symmetry for compounds 7–10, while C2 turned out to be that for 5 and 6. Fig. 3 shows the most stable structures for 7–10 calculated by B3LYP/def2-TZVPP, [twist angles δ: (7) 0.1°, (8) 6.2°, (9) 3.8°, (10) 55.0°]. Table 4 shows the most stable structures with relative energies of 0.00 kcal/mol compared with the rest of structures that are higher in energy. Hexacoordinated molybdenum(VI) compounds may stabilize either distorted octahedral or trigonal prismatic geometry around the metal center, most compounds reported in the literature present trigonal prismatic geometry. We did calculations to find out the energy difference between both structures, the results indicated that the latter is more stable.

The lowest energy optimized structures of molybdenum(VI) complexes 7–9 show a preference for trigonal prismatic against distorted octahedral geometry, as shown in Table 5, in which a comparison with crystal structures of analogous MoVI complexes containing bidentate ligands. The presence of two different donor atoms (S, O, N) in each of the ligands allows them to coordinate as bidentate ligands. The bond lengths and angles [Mo–X, S–Mo–X (X = S, O, N)] are as expected for trigonal prismatic geometry. It is worth mentioning that there is also a coincidence when comparing with mean inter- and intra-ligand distances [S–X, (X = S, O, N)], which are smaller than the sum of the van der Waals radii for S...S = 3.6 Å, S...O = 3.35 Å and S...N = 3.4 Å [54]. Additional calculations were to investigate the existence of intramolecular interactions, since these interactions stabilize the trigonal structure according to other reports [24–26], Fig. 4. The results obtained in these studies are explained in terms of the electronic properties of sulfur, and its ability to use the 3d orbitals [41]. The additional calculations performed herein include NBO analysis and visualization of molecular orbitals; the results obtained do not show any intramolecular interactions between S–X atoms (X = S, N and O), since the distances between these atoms are larger than the sum of the Van der Waals radii. For compound 10, the aliphatic bidentate ligand coordinated to molybdenum has a higher degree of rotational freedom and adopts a distorted octahedral geometry. The chelate ring formed by molybdenum and the bidentate ligand is almost planar in all cases.

Fig. 5 shows the lowest energy structures for compounds 11 and 12, the observed geometry corresponds to a distorted octahedron in both cases, whose point group is C2 [S–Mo=O angles: (11) 161.3°, (12) 168.2°; twist angles δ: (11) 2.9°; (12) 25.6°]. The Mo–S distances [(11) 2.75 Å, (12) 3.57 Å] are smaller than the sum of the van der Waals radii of (Mo–S = 3.9 Å) and larger than that of the covalent radii (Mo–S = 2.4 Å) confirming Mo-S coordination [54]. The S–Mo–S angles [(11) 80.6°, (12) 97.7°] and intra-ligand S–S distances [(11) 3.56 Å, (12) 5.38 Å] are in good agreement with the high affinity of sulfur towards molybdenum.

5. Conclusions

A series of molybdenum complexes (7–12) was synthesized. Calculations in vacuo showed a slight preference for C3 (7–10) and C2 (11,12) symmetries, which were the lowest energy optimized structures obtained by density functional theory in gas-phase. Trigonal prismatic geometry is preferred in solid state for
the tris-chelate complexes, in agreement with results for similar compounds; it is thought after this study, that this is also the case in solution as indicated by the NMR results and in the gas-phase by electronic methods (B3LYP/def2-TZVPP). S–S inter-ligand interactions may be of utmost importance in determining the geometry of the complexes, this property can be extended to the S–O and S–N interactions.

Acknowledgments

Thanks to DGAPA-UNAM for postdoctoral scholarship of R.C.-P. and CONACYT (Grant VI-060894-CB) for financial support. We acknowledge A. Vásquez Badillo to Prof. M. E. Sosa-Torres and CONACyT (Grant VI-060894-CB) for financial support.

References

[31] A. Vásquez Badillo to Prof. M. E. Sosa-Torres and CONACyT (Grant VI-060894-CB) for financial support. We acknowledge A. Vásquez Badillo to Prof. M. E. Sosa-Torres and CONACyT (Grant VI-060894-CB) for financial support.