

## SIX-COORDINATE MOLYBDENUM(II) COMPLEXES OF 2,2'-BIPYRIDINE CONTAINING THIOLATE, NITRATE, NITRITE AND PENTANE-2,4-DIONATE LIGANDS

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### Summary

Substitution of 2,2'-bipyridine (bipy) in the seven-coordinate molybdenum(II) salt *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub> by sodium 1,1-dimethylethanethiolate gives six-coordinate red *trans,cis*-[Mo(SCMe<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>(bipy)] and by sodium *N,N*-diethyldithiocarbamate gives purple *cis*-[Mo(CO)<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)(bipy)][BF<sub>4</sub>]. Tetrabutylammonium nitrate also displaces bipy to form green *cis*-[Mo(η<sup>2</sup>-NO<sub>3</sub>)(CO)<sub>2</sub>(bipy)][BF<sub>4</sub>]. Substitution of CO in the same seven-coordinate molybdenum(II) salt by nitrite produces green [Mo(ONO)(CO)(bipy)<sub>2</sub>][BF<sub>4</sub>], and by pentane-2,4-dione (acacH) gives purple [Mo(acac)(bipy)<sub>2</sub>][BF<sub>4</sub>]. The products of the reactions have been characterised by microanalysis and IR, <sup>1</sup>H NMR, and electronic absorption spectroscopy.

### Introduction

The seven-coordinate molybdenum(II) cation, [Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)]<sup>2+</sup> reacts with various neutral nucleophiles such as isocyanides and tertiary phosphines so that displacement of coordinated acetonitrile and of CO occurs rather than that of 2,2'-bipyridine. Seven-coordination of the metal atom is maintained in the products of these reactions [1]. We report the reactions of the same molybdenum(II) cation with anionic nucleophiles containing harder donor atoms (S, O), which produce six-coordinate products.

### Results and discussion

The molybdenum(II) salt *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub> (1 mol) in acetonitrile solution reacts rapidly with solid NaSCMe<sub>3</sub> (2 mol) at room tempera-

ture to form a red-brown complex,  $[\text{Mo}(\text{SCMe}_3)_2(\text{CO})_2(\text{bipy})]$ ; addition of excess thiolate caused no further substitution under these conditions. The thiolate complex is soluble in dichloromethane, acetone and acetonitrile, and slightly soluble in diethyl ether and in hexane. The complex is characterised by two strong infrared absorptions ( $1940, 1820 \text{ cm}^{-1}$ ) assigned to CO ligand stretching vibrations. The  $^1\text{H}$  NMR spectrum of the diamagnetic complex contains a single sharp resonance ( $\delta$  1.63 ppm in  $\text{CD}_2\text{Cl}_2$ ) which is assigned to the two equivalent *t*-butyl groups, as well as four signals from the protons of the bipy ligand. These observations establish the stereochemistry of the complex as *trans,cis*- $[\text{Mo}(\text{SCMe}_3)_2(\text{CO})_2(\text{bipy})]$ . This complex can be compared with *trans,cis*- $[\text{Mo}(\text{OCMe}_3)_2(\text{CO})_2(\text{pyr})_2]$ , which is produced in the reaction of CO with  $[\text{Mo}_2(\text{OCMe}_3)_6]$  in hexane/pyridine solvent mixtures [2]. The low frequencies of the CO ligand stretching absorptions ( $1908, 1768 \text{ cm}^{-1}$ ) and their separation ( $140 \text{ cm}^{-1}$ ), together with the acute CMoC angle ( $72.4^\circ$ ) in the alkoxide complex have been interpreted in terms of the  $\pi$ -donor action of the *t*-butoxy ligands. [2] The values of  $\nu(\text{CO})$  in *trans,cis*- $[\text{Mo}(\text{SCMe}_3)_2(\text{CO})_2(\text{bipy})]$  are higher and their separation is less than in the alkoxide complex. This may reflect the fact that the bipy ligand, which is constrained to be coplanar with the CO ligands, is a better  $\pi$ -acceptor than pyridine which is not so constrained. The structure of *trans,cis*- $[\text{Mo}(\text{OCMe}_3)_2(\text{CO})_2(\text{pyr})_2]$  shows that, in the solid state, the pyridine ring planes are both approximately orthogonal to the  $\{\text{Mo}(\text{CO})_2\}$  plane [2]. Further, the values of  $\nu(\text{CO})$  in *trans,cis*- $[\text{Mo}(\text{SCMe}_3)_2(\text{CO})_2(\text{bipy})]$  are close to those [2] in  $[\text{Mo}_2(\text{OCHMe}_2)_4(\text{CO})_2]$  which is consistent with a net increase in effective nuclear charge at molybdenum in *trans,cis*- $[\text{Mo}(\text{SCMe}_3)_2(\text{CO})_2(\text{bipy})]$  compared to *trans,cis*- $[\text{Mo}(\text{OCMe}_3)_2(\text{CO})_2(\text{pyr})_2]$ .

The diamagnetism of the six-coordinate complex *trans,cis*- $[\text{Mo}(\text{SCMe}_3)_2(\text{CO})_2(\text{bipy})]$  is consistent with that of *trans,cis*- $[\text{Mo}(\text{OCMe}_3)_2(\text{CO})_2(\text{pyr})_2]$ , that the presence of the  $\pi$ -donor ligands causes a lifting of the degeneracy of the  $t_{2g}$  orbitals. This is in contrast to the paramagnetism of *cis*- $[\text{Mo}(\text{OCHMe}_2)_2(\text{bipy})_2]$ , which exists in an equilibrium between singlet and triplet spin states [3].

Other examples of six-coordinate molybdenum(II) thiolate complexes include  $[\text{Mo}(\text{SR})_2(\text{dppe})_2]$  ( $\text{R} = n\text{-C}_4\text{H}_9, n\text{-C}_3\text{H}_7$ ) [4] and  $[\text{Mo}(\text{SCMe}_3)_2(\text{CNCMe}_3)_4]$  [5].

Addition of an equimolar proportion of sodium *N,N*-diethyldithiocarbamate in acetonitrile solution to a well-stirred solution of *cis*- $[\text{Mo}(\text{CO})_2(\text{bipy})_2(\text{NCMe})][\text{BF}_4]_2$  in the same solvent at room temperature produces a purple solution from which a purple solid is isolated on concentration. This purple crystalline solid is identified as *cis*- $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)(\text{bipy})][\text{BF}_4]$  by microanalysis and spectroscopy. The infrared spectrum shows two strong absorptions ( $1940, 1855 \text{ cm}^{-1}$ ) assigned to *cis*-carbonyl ligands. Addition of a further mole of sodium *N,N*-diethyldithiocarbamate in acetonitrile to a solution of *cis*- $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)(\text{bipy})][\text{BF}_4]$  in the same solvent produced a deep red solution from which *cis*- $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2]$  was isolated as red-purple crystals. The six-coordinate *cis*- $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2]$  is well-known [6]; it can bind CO to give  $[\text{Mo}(\text{CO})_3(\text{S}_2\text{CNEt}_2)_2]$  reversibly [7]. The selectivity with which these complexes are formed is emphasised by the fact that we have been unable to prepare the *cis*- $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)(\text{bipy})]^-$  ion either by reaction of *cis*- $[\text{Mo}(\text{CO})_4(\text{bipy})]$  with  $\text{Na}[\text{S}_2\text{CNEt}_2]$  or by reaction between  $[\text{Mo}(\text{CO})_3(\text{S}_2\text{CNEt}_2)_2]$  and 2,2'-bipyridine. The fact that *cis*- $[\text{Mo}(\text{CO})_3(\text{S}_2\text{CNEt}_2)_2(\text{NCMe})]$  is not isolated from the reaction between  $[\text{Mo}(\text{CO})_3(\text{bipy})_2(\text{NCMe})][\text{BF}_4]_2$  and sodium *N,N*-diethyldithiocarbamate is consistent with the easy loss of CO from

[Mo(CO)<sub>3</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] [7] and the fact that [Mo(CO)(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>(bipy)] is not formed in preference to *cis*-[Mo(CO)<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>].

The <sup>1</sup>H NMR spectra of *cis*-[Mo(CO)<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)(bipy)][BF<sub>4</sub>] and *cis*-[Mo(CO)<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] both show inequivalent ethyl proton resonances. This may be explained by the low symmetry of the two six-coordinate complexes. The multiplet signal of bipy-H(3) in *cis*-[Mo(CO)<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)(bipy)][BF<sub>4</sub>] (δ 9.05 ppm) appears to low field of the H(6) signal (δ 8.85 ppm); this unusual arrangement (δ(H(3)) > δ(H(6))) has also been observed [1] in the spectra of other molybdenum(II) complexes, [Mo(CNEt)<sub>3</sub>(bipy)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> and *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub>.

Tetra(*n*-butyl)ammonium nitrate reacts with an equimolar quantity of *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>] in acetonitrile solution at room temperature to produce a high yield (74%) of a dark green complex, identified as *cis*-[Mo(η<sup>2</sup>-NO<sub>3</sub>)(CO)<sub>2</sub>(bipy)][BF<sub>4</sub>] by microanalysis and spectroscopy. The infrared spectrum shows two strong absorptions (1820, 1720 cm<sup>-1</sup>) assigned to *cis* carbonyl ligands. The nitrate group is recognised by absorptions at 1495s, 1340m and 1250m,sh cm<sup>-1</sup>. The nitrate absorption which might be expected at ca. 1030 cm<sup>-1</sup> is obscured by the strong, broad absorption of the tetrafluoroborate ion. The <sup>1</sup>H NMR spectrum of the complex (acetone-*d*<sub>6</sub> solution) contains the four signals (δ 7.42 (H(5)), 8.12 H(4)), 8.40 (H(3)), 9.05 (H(6)) ppm) of the bipy ring protons. These data suffice to characterise the dark green cation and to identify it with cation in the minor product of the oxidation of *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>] with Ag[NO<sub>3</sub>], which is *cis*-[Mo(η<sup>2</sup>-NO<sub>3</sub>)(CO)<sub>2</sub>(bipy)][NO<sub>3</sub>]. The major product of the silver(I) nitrate oxidation has been identified as [Mo(NO<sub>3</sub>)(CO)<sub>2</sub>(bipy)<sub>2</sub>][NO<sub>3</sub>] [8].

The equimolar addition of tetraethylammonium nitrite in acetonitrile solution to *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub> in the same solvent caused an immediate change in colour to dark green with the formation of the product which is identified as six-coordinate [Mo(ONO)(CO)(bipy)<sub>2</sub>][BF<sub>4</sub>] by microanalysis and spectroscopy. The single carbonyl ligand is indicated by a strong absorption at 1890 cm<sup>-1</sup> and the O-bonded nitrito ligand by absorptions at 1440s, 1160m, and 890m cm<sup>-1</sup>; the absence of an absorption in the 1340–1320 cm<sup>-1</sup> region [9] precludes the *N*-bonded nitro form. The complex is a 1 : 1 electrolyte in acetonitrile solution. The observation of a well-resolved <sup>1</sup>H NMR spectrum in solution is consistent with diamagnetism. The simplicity of the NMR spectrum may suggest a *trans*-stereochemistry of the carbonyl and nitrito ligands, but previous experience of several *cis*-bis(2,2'-bipyridine) complexes of molybdenum(0) and molybdenum(II) which also show fortuitously simple <sup>1</sup>H NMR spectra [1,8,10], indicates the need for caution in the absence of an X-ray crystallographic structure determination.

The reaction between equimolar proportions of sodium pentane-2,4-dionate, Na[acac], and *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub> in acetonitrile at room temperature is rapid and produces a dark purple (black) solution from which purple-black crystals can be isolated. The same material can be produced when an excess of pure pentane-2,4-dione, acacH, is warmed (320 K) with *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub> in acetonitrile. The purple-black solid is characterised as [Mo(acac)(bipy)<sub>2</sub>][BF<sub>4</sub>] by microanalysis and spectroscopy. The infrared spectrum of the complex establishes that the acac ligand is O-bonded (ν(CO) 1560m, 1530vs cm<sup>-1</sup>), and this is confirmed by the <sup>1</sup>H NMR spectrum in which the methyl protons produce a signal at δ 2.15 and the γ-methine proton resonates at δ 5.65 ppm.

## Conclusions

The substitution reactions between anionic nucleophiles and the seven-coordinate molybdenum(II) dication,  $cis-[Mo(CO)_2(bipy)_2(NCMe)]^{2+}$  have indicated a number of interesting and, to some extent, surprising differences when compared with the substitution reactions produced by neutral nucleophiles. The products of anionic nucleophile substitution are all six-coordinate, diamagnetic molybdenum(II) complexes, whereas neutral nucleophiles (phosphines, phosphites, isocyanides) generally lead to conservation of seven-coordination in the product [11]. The neutral nucleophiles displace the coordinated ligands in the descending order of preference: MeCN(solvent) > CO > bipy [11]. We find that the anionic nucleophiles we have used here all displace the solvent and then may displace either bipy, in the case of the thiolate nucleophiles (MeCS<sup>-</sup>, Et<sub>2</sub>NCS<sub>2</sub><sup>-</sup>) and nitrate, or carbon monoxide, in the case of nitrite and pentanedionate. This distinction appears to be based on the hardness [12] of the nucleophile.

## Experimental

Preparations were all carried out under pre-purified dinitrogen using standard techniques (Schlenk-types apparatus, cannulae, vacuum manifold). All solvents were dried (calcium hydride, sodium, or molecular sieves), deaerated and distilled before use. The preparation of  $cis-[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$  has been described in detail [1]. 1,1-Dimethylethanethiol and pentane-2,4-dione were purchased from Aldrich. Tetraethylammonium nitrite was freshly prepared by the addition of silver(I) nitrite to tetraethylammonium chloride in acetonitrile solution. Other reagents were purchased in the highest available purity and were used as received without further purification. Conductivity measurements were made with a Wayne Kerr bridge B221; the cell constant of the glass conductivity probe was calculated from measurements using standardised 0.01 mol dm<sup>-3</sup> potassium chloride solution. IR spectra were recorded on a Perkin-Elmer PE625 spectrometer. NMR spectra were recorded on a JEOL PS100 spectrometer. Electronic absorption spectra were measured on a Perkin-Elmer PE402 spectrometer. Microanalyses were performed by Mr. A. Fassam.

### Preparations

#### *trans,cis-[Bis(1,1-dimethylethaneethiolato)dicarbonyl(2,2'-bipyridine)molybdenum(II)]*

Freshly prepared solid sodium 1,1-dimethylethanethiolate (0.39 g, 3.56 mmol) was added in small portions to a rapidly stirred solution of  $cis-[Mo(CO)_2(bipy)_2(NCMe)][BF_4]_2$  (1.21 g, 1.78 mmol) in acetonitrile (40 cm<sup>3</sup>). The colour of the reaction mixture became red-brown immediately. The mixture was stirred for 0.5 h and then extracted with dichloromethane, filtered and petroleum ether (40–60°C) was allowed to diffuse into the filtrate. A finely divided red-brown powder separated during several days. This was isolated by filtration, washed with petroleum ether (40–60°C) and then dried in vacuo (0.43 g, 50% yield). (Found: C, 49.8; H, 6.5; N, 5.5; S, 14.5. C<sub>20</sub>H<sub>34</sub>MoN<sub>2</sub>O<sub>2</sub>S<sub>2</sub> calcd.: C, 49.4; H, 6.9; N, 5.8; S, 13.2%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.41 (td, H(5)), 8.03 (dd, H(4)), 8.43 (d, H(3)), 9.17 (d, H(6)).

1.63 (s, 9H, CMe<sub>3</sub>) ppm. IR (Nujol) 1600m, 1420s, 1380m, 1250m, 1150s, 970m cm<sup>-1</sup>. λ<sub>max</sub> (MeCN) 515 nm.

*cis*-[*N,N*-Diethyldithiocarbamato]dicarbonyl(2,2'-bipyridine)molybdenum(II)tetrafluoroborate

A solution of sodium *N,N*-diethyldithiocarbamate (0.34 g, 1.97 mmol) in acetonitrile (10 cm<sup>3</sup>) was added slowly (syringe) to a stirred solution of *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub> (1.34 g, 1.97 mmol) in acetonitrile (30 cm<sup>3</sup>). The mixture rapidly became purple in colour. After being stirred for 1 h at room temperature the mixture was evaporated to dryness under reduced pressure. The solid residue was extracted with dichloromethane and the extract was filtered. Petroleum ether (40–60°C) was allowed to diffuse into the filtrate. After 3 d purple crystals were isolated by filtration, washed with diethyl ether and dried in vacuo (0.97 g, 90% yield). (Found: C, 36.9; H, 3.0; N, 8.3; S, 11.2. C<sub>17</sub>H<sub>18</sub>BF<sub>4</sub>MoN<sub>3</sub>O<sub>2</sub>S<sub>2</sub> calcd.: C, 37.6; H, 3.3; N, 7.7; S, 11.7%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 1.35 (tt, CH<sub>3</sub>), 3.95 (sextet, CH<sub>2</sub>), 7.60 (td, H(5)), 8.14 (td, H(4)), 8.85 (d, H(6)), 9.05 (d, H(3)) ppm. IR (Nujol) 1940s, 1855s, 1600m, 1500m, 1310w, 1280w, 1055sbr, 980s cm<sup>-1</sup>. λ<sub>max</sub> (MeCN) 500 nm.

*cis*-[(η<sup>2</sup>-Nitrato)dicarbonyl(2,2'-bipyridine)molybdenum(II)] tetrafluoroborate

Tetra(n-butyl)ammonium nitrate (0.56 g, 1.84 mmol) in acetonitrile solution (10 cm<sup>3</sup>) was added slowly (syringe) to a rapidly stirred solution of *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub> (1.25 g, 1.84 mmol) in acetonitrile (30 cm<sup>3</sup>). The reaction mixture rapidly became dark green in colour. The mixture was stirred at room temperature for 1 h and then filtered. The filtrate was evaporated to dryness under reduced pressure. The solid residue was extracted with acetone (20 cm<sup>3</sup>) and the extract was filtered. Diethyl ether was allowed to diffuse into the extract so that the precipitation of a green solid occurred over a period of several days. The green powder was isolated by filtration and then washed with diethyl ether and finally dried in vacuo. (0.62 g, 74% yield). (Found: C, 31.3; H, 2.0; Mo, 20.7; N, 9.0. C<sub>12</sub>H<sub>8</sub>BF<sub>4</sub>MoN<sub>3</sub>O<sub>5</sub> calcd.: C, 31.5; H, 1.7; Mo, 21.0; N, 9.2%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 7.42 (td, H(5)), 8.12 (td, H(4)), 8.49 (d, H(3)), 9.05 (d, H(6)) ppm. IR (Nujol) 1820s, 1720s, 1600m, 1495s, 1320m, 1280w, 1250m, 1055br, 940m, 910m, 770s cm<sup>-1</sup>. λ<sub>max</sub> (MeCN) 430 nm.

Nitrocarbonylbis(2,2'-bipyridine)molybdenum(II) tetrafluoroborate

Tetraethylammonium nitrite (0.31 g, 1.76 mmol) in acetonitrile (10 cm<sup>3</sup>) was added slowly (syringe) to a rapidly stirred solution of *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub> (1.18 g, 1.74 mmol) in acetonitrile (30 cm<sup>3</sup>). The reaction mixture rapidly became dark green in colour. The mixture was stirred at room temperature for 3 h and then filtered. The filtrate was evaporated to dryness under reduced pressure. The solid residue was extracted with acetone and the extract was filtered. Diethyl ether was allowed to diffuse into the extract, so that the precipitation of a finely divided green solid occurred over a period of 3 d. The green powder was isolated by filtration, then washed with diethyl ether and finally dried in vacuo (0.32 g, 32% yield). (Found: C, 44.4; H, 2.7; N, 12.3. C<sub>21</sub>H<sub>16</sub>BF<sub>4</sub>MoN<sub>5</sub>O<sub>3</sub> calcd.: C, 44.3; H, 2.8; N, 12.3%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 7.57 (t, H(5)), 8.18 (t, H(4)), 8.49 (d, H(3)), 8.95(d, H(6)) ppm. IR (Nujol) 1890 vs, 1595m, 1440s, 1320w, 1260w, 1180m, 1160m, 1055br, 780s cm<sup>-1</sup>. λ<sub>max</sub> (MeCN) 605 nm.

*Pentane-2,4-dionatobis(2,2'-bipyridine)molybdenum(II) tetrafluoroborate*

Pentane-2,4-dione (0.35 g, 3.5 mmol) was added to *cis*-[Mo(CO)<sub>2</sub>(bipy)<sub>2</sub>(NCMe)][BF<sub>4</sub>]<sub>2</sub> (0.79 g, 1.16 mmol) in acetonitrile (30 cm<sup>3</sup>). The mixture was heated at 320 K for 1 h. The mixture was then cooled and evaporated to dryness under reduced pressure. The solid residue was dissolved in acetone and the solution was filtered. Diethyl ether was allowed to diffuse into the purple filtrate and purple-black crystals were formed over a period of 3 d. These crystals were isolated by filtration, then washed with diethyl ether and finally dried in vacuo (0.37 g, 53% yield). (Found: C, 50.1; H, 3.6; N, 9.8. C<sub>25</sub>H<sub>23</sub>BF<sub>4</sub>MoN<sub>4</sub>O<sub>2</sub> calcd.: C, 50.5; H, 3.8; N, 9.4%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>CN) δ 2.15 (s, 6H, CH<sub>3</sub>), 5.65 (s, 1H, CH), 7.85 (t, H(5)), 8.50 (dd, H(4)), 8.85 (d, H(3)), 8.95 (d, H(6)) ppm. IR (Nujol) 1610m, 1560m, 1530s, 1345s, 1320m, 1290m, 1250w, 1170m, 1055br, 769s, 730s cm<sup>-1</sup>.

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**References**

- 1 J.A. Connor, E.J. James, C. Overton and N. El Murr, *J. Chem. Soc., Dalton Trans.*, (1984) 255.
- 2 M.H. Chisholm, J.C. Huffman and R.L. Kelly, *J. Am. Chem. Soc.*, 101 (1979) 7615.
- 3 M.H. Chisholm, E.M. Kober, D.J. Ironmonger and P. Thornton, *Polyhedron*, 4 (1985) 1869.
- 4 J. Chatt, J.P. Lloyd and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1976) 565.
- 5 M. Kamata, K. Hirotsu, T. Higuchi, K. Tatsumi, R. Hoffmann, T. Yoshida, and S. Otsuka, *J. Am. Chem. Soc.*, 103 (1981) 5772.
- 6 R. Colton, G.R. Scollary and I.B. Tomkins, *Aust. J. Chem.*, 21 (1968) 15; J.L. Templeton and B.C. Ward, *J. Am. Chem. Soc.*, 102 (1980) 6568; S.J.N. Burgmayer and J.L. Templeton, *Inorg. Chem.*, 24 (1985) 2224.
- 7 R. Colton and G.R. Scollary, *Aust. J. Chem.*, 21 (1968) 1427.
- 8 J.A. Connor and E.J. Jones, *J. Organomet. Chem.*, 297 (1985) 301.
- 9 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Third Edition. Wiley, Chichester, 1978.
- 10 J.A. Connor and C. Overton, *J. Chem. Soc., Dalton Trans.*, (1982) 2397; M.H. Chisholm, J.A. Connor, J.C. Huffman, E.M. Kober and C. Overton, *Inorg. Chem.*, 23 (1984) 2298.
- 11 J.A. Connor, E.M. Jones, C. Overton, J.M.A. Walshe and R.A. Head, *J. Chem. Soc., Dalton Trans.*, (1986) 511.
- 12 W.W. Porterfield, *Inorganic Chemistry, A Unified Approach*. Addison Wesley Reading, 1984, p. 245.