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**SYNTHESIS AND CHARACTERIZATION
OF *trans*-Mo(CO)₄(*p*-C₅NH₄SO₃Na)₂**

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Abstract

Reaction between Mo(CO)₆ and *p*-C₅NH₄SO₃Na (1:2 (Mo: *p*-C₅NH₄SO₃Na) stoichiometric ratio) gave the *trans*-Mo(CO)₄(*p*-C₅NH₄SO₃Na)₂ complex, (1), in 80% yield. Complex (1) has been characterized by FTIR, ¹H and ¹³C NMR spectroscopy. Complex (1) has most likely an idealized D_{4h} geometry with *trans* N-bound *p*-C₅NH₄SO₃Na ligands.

Keywords: Molybdenum, pyridine-*p*-sulphonate, carbonyl complexes

INTRODUCTION

The coordination and organometallic chemistry of molybdenum is one of the most varied, complex and interesting of the transition metals. Practical applications of Mo complexes are numerous, including industrial and laboratory catalytic processes [1-3]. Mo(CO)₆, is an important industrial compound, and a

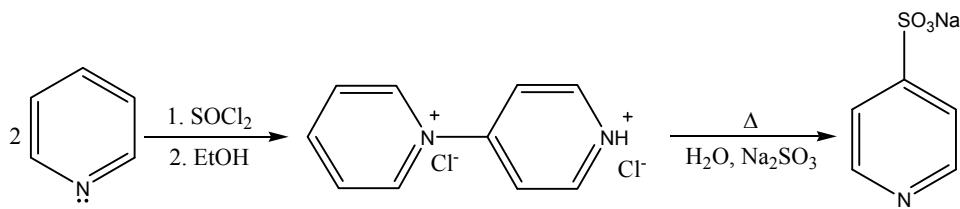
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very useful starting point for new Mo complexes. In our laboratory we have used it to synthesize $\text{mer-Mo(CO)}_3(p\text{-C}_5\text{NH}_4\text{CN})_3$ [4-5] and now we report the synthesis and characterization of complex (**1**).

EXPERIMENTAL

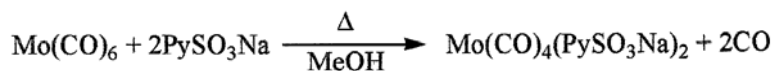
Materials and methods

Reagents: SOCl_2 , pyridine, Na_2SO_3 , (Aldrich), Mo(CO)_6 (Strem), Ar (Gases Industriales de Venezuela) were obtained commercially and used as received. MeOH and other organic solvents were purified as described in the literature [6].



Scheme 1. Synthesis of (*p*-PySO₃Na)

Synthesis of sodium 4-pyridylsulfonate (p-PySO₃Na). The synthesis is shown in Scheme 1. The intermediate N-(4-pyridyl)pyridinium chloride hydrochloride is synthesized as follows: Pyridine (41.2 g, 0.52 mol) is placed into a 250 mL flask, cooled in an ethanol bath to -5°C , and thionyl chloride (108.77 g, 0.91 mol) is slowly added. After thionyl chloride addition, a drying tube is placed and the solution is allowed to stand at room temperature for 3 days; the solution changes from pale yellow to dark brown. The excess SOCl_2 is carefully distilled, leaving a dark solution; this solution is cooled to 0°C and ethanol (50 mL) is slowly added to eliminate traces of SOCl_2 . The dark solid obtained from this solution is used to produce *p*-PySO₃Na as follows: the intermediate N-(4-pyridyl)pyridinium chloride hydrochloride (23 g, 0.1 mol) is dissolved in water (150 mL) in a two-necked flask, and sodium sulfite (76.5 g, 0.61 mol) is slowly added until no more SO_2 is evolved. The solution is refluxed for 24 hours under inert atmosphere, slowly cooled and activated carbon (4 g) is added, and refluxed for one more hour. The solution is filtered and evaporated to dryness. The dark solid is Soxhlet extracted with ethanol (250 mL) for 24 hours. The ethanol extract is reduced in volume and cooled; beige crystalline solid precipitates (70% yield), 180°C melting point; soluble in H_2O , MeOH and CHCl_3 .



Scheme 2. Synthesis of *trans*-Mo(CO)₄(*p*-PySO₃Na)₂ (1)

Synthesis of trans-Mo(CO)₄(p-PySO₃Na)₂: The synthesis is shown in Scheme 2. To Mo(CO)₆ (0.1 g, 0.38 mmol) in refluxing MeOH (50 mL), *p*-PySO₃Na (0.13 g, 0.72 mmol) dissolved in MeOH (20 mL) is slowly added, and allowed to reflux for 4 hours; the solution changes to reddish yellow, which is allowed to cool, and the volume reduced under vacuum and cooled, giving a greenish yellow solid (80% yield); 186-190°C melting point, soluble in H₂O, MeOH and EtOH.

Physical measurements: UV-visible electronic absorption spectrum in water solution was recorded in a LAMBDA 3 Perkin-Elmer spectrophotometer. Vibrational spectrum (5000-400 cm⁻¹, KBr pellet) was taken in a Fourier Transform Perkin-Elmer 1725X spectrophotometer. Room temperature ¹H and ¹³C nuclear magnetic resonance spectra (*DMSO-d₆*, solutions, TMS internal standard) were taken in a Bruker Avance DRX 400-MHz spectrometer.

RESULTS AND DISCUSSION

Sodium 4-pyridinsulphonate (p-PySO₃Na) Characterization: The FTIR spectrum shows characteristic bands due to the sulphonate group and the pyridine ring (cm⁻¹): ν(C-S) 1411 (medium, sharp); ν(S=O) 1222 (strong, sharp); ν(C=C) 1590 (weak); ν(C=N) 1660 (medium, sharp); ν(C-H) 3046 (weak). The ¹H NMR spectrum has the following peaks (see Diagram 1, (a)); δ(ppm): 7.75 [H^b, doublet, 2H, J_{Hbc} = 6.26 Hz]; 8.70 [H^c, doublet, 2H, J_{Hbc} = 6.21Hz]; ¹³C NMR shows the following peaks (see Diagram 1 (b)); δ(ppm) 150 [C^a, singlet]; 119 [C^b, singlet]; 149 [C^c, singlet].

trans-Mo(CO)₄(p-PySO₃Na)₂ (1) Characterization: The FTIR spectrum shows the following characteristic bands (see Fig. 1, KBr, cm⁻¹): ν(C=O) 1922 (band 1, strong, broad); ν(C=N) 1647 (2, weak, broad); ν(C=C) 1584 (3, medium, sharp); ν(C-S) 1410 (4, strong, sharp); ν(S=O) 1222 (5, strong, broad); ν(C-H) 3049 (6, weak, sharp). The 3470 cm⁻¹ (strong, broad) band corresponds to the hydration sphere of the sulphonate group. We propose a *trans*-Mo(CO)₄(*p*-PySO₃Na)₂ six coordinated structure (ideal D_{4h} symmetry, see Diagram 2), which is corroborated by a simple group theory comparison of the ν(CO) modes with the possible *cis*-Mo(CO)₄(*p*-PySO₃Na)₂ isomer. For the *trans*

isomer one strong e_u IR active band is predicted as shown for analogous Mo complexes [7], while the cis isomer should give four IR active bands. The ^1H NMR spectrum of (1) has the following peaks (see Diagram 2 (a)), $\delta(\text{ppm})$: 7.77 [H^b , doublet, 2H, $J_{\text{Hbc}} = 5.01$ Hz]; 8.72 [H^c , doublet, 2H, $J_{\text{Hbc}} = 5.14$ Hz]; ^{13}C NMR shows the following peaks (see Diagram 2 (b), $\delta(\text{ppm})$): 151 [C^a , singlet]; 119.8 [C^b , singlet]; 149 [C^c , singlet]; 186 [C^d , singlet].

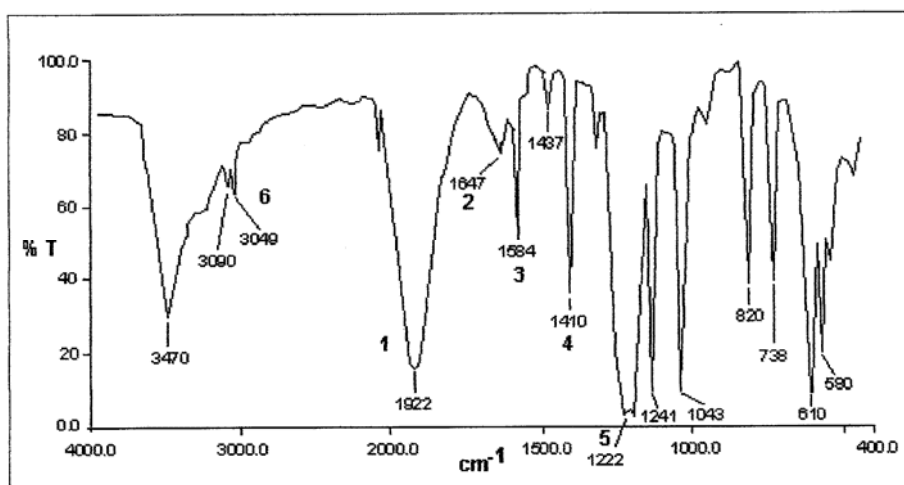


Fig. 1. FTIR spectrum (KBr) of the *trans*- $\text{Mo}(\text{CO})_4(p\text{-PySO}_3\text{Na})_2$, (1)

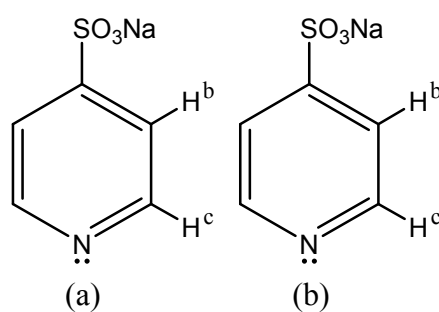


Diagram 1. Proposed structure for the ligand (*p*-PySO₃Na) according to (a) ^1H NMR. (b) ^{13}C NMR

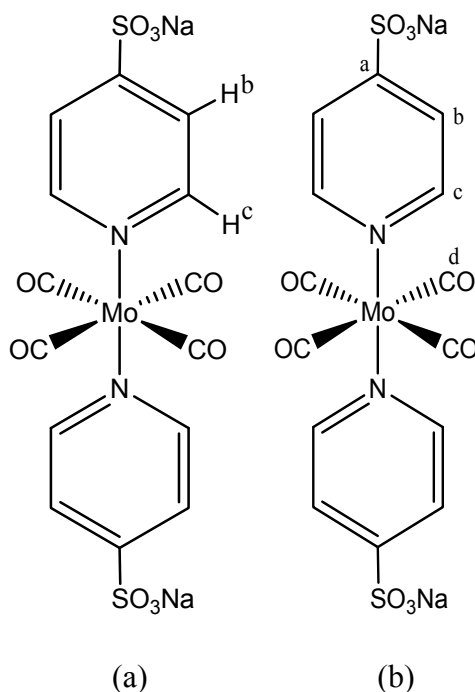


Diagram 2. Proposed structure for complex **(1)**, $trans\text{-Mo(CO)}_4(p\text{-PySO}_3\text{Na})_2$ according to (a) ^1H NMR (b) ^{13}C NMR

CONCLUSIONS

The water soluble ligand ($p\text{-PySO}_3\text{Na}$) was synthesized in a good yield. The new water-soluble $trans\text{-Mo(CO)}_4(p\text{-PySO}_3\text{Na})_2$ (Complex 1), was synthesized in a good yield, and characterized by IR and NMR measurements. An idealized D_{4h} trans structure is proposed.

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REFERENCES

1. T. Kawai, M. Komaki, T. Iyoda: *J. Mol. Catal. Chem.*, **190**, 45 (2002).
2. G.C. Bazan, E. Khosravi, R.R. Schrock, W.J. Feast, V.C. Gibson, M.B. O'Regan, J.K. Thomas, W.M. Davis: *J. Am. Chem. Soc.*, **112**, 8378 (1990).
3. R.H. Grubbs, S. Chang: *Tetrahedron*, **54**, 4413 (1998).

4. M. Parra, T. Suárez, B. Fontal, M. Reyes, F. Bellandi, I. Romero, P. Cancines: 3° *Encuentro de Química Inorgánica 2007*, Guanajuato, Gto -México, August 15-17, 020 (2007).
5. T. Suárez, M.F. Parra, B. Fontal, R.R. Contreras, M. Reyes, F. Bellandi, Y. Fonseca, P. Cancines: 4° *Congreso de Catálisis del MERCOSUR*, La Plata-Argentina, November, 12-16, ID-015 (2007).
6. A.J. Gordon, R.A. Ford: *The Chemist's Companion*, p. 434. Wiley, New York 1972.
7. K.F. Purcell, J.C. Kotz: *Inorganic Chemistry*, p. 901-2. W.B. Saunders Co, PA, 1977.