Journal of Organometallic Chemistry, 463 (1993) 121–125

JOM 23702

Heterobimetallic Mo–Sn complexes with seven-coordinate molybdenum and five-coordinate tin

Mercedes Cano [a], Margarita Panizo [a], José Antonio Campo [a], Jesús Tornero [b] and Nieves Menéndez [b]

[a] *Departamento de Química Inorgánica I, Facultad de C. Químicas, Universidad Complutense de Madrid, 28040-Madrid (Spain)*
[b] *Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, 28049-Madrid (Spain)*

(Received January 25, 1993)

Abstract

New heterobimetallic complexes $[Mo(SnRCl_2)(CH_3CN)_2(CO)_3(Cl)]$ [(1)R = C_6H_5, (2) R = CH_3] have been obtained by reaction of $[Mo(CH_3CN)_3(CO)_3]$ and $SnRCl_3$. The reactions may be considered as insertion of $[Mo(CH_3CN)_2(CO)_3]$ into the Sn–X bond of the organotin halides. The IR and ^1H, ^{13}C NMR spectra of the isolated products are consistent with heptacoordination around the molybdenum, produced by three *facial* carbonyl groups and two *cis*-MeCN, and the other two positions occupied by Cl and $SnRCl_2$. Mössbauer spectroscopy data are consistent with the presence of a pentacoordinate environment at tin with a Mo–Sn bond bridged by a chloride atom. The complexes change in solution and intermediates are detected by IR and NMR spectroscopies when coordinating solvents are employed. The thermal behaviour in solution is also reported.

1. Introduction

The involvement of seven-coordinate Mo or W complexes in some catalytic processes [1–3] has encouraged research into related heterobimetallic compounds. Some M–Sn (M = Mo or W) derivatives of the type $[M(CO_3)L_2(X)(SnRX_2)]$ (M = Mo; L_2 = bipy; R = Cl), (M = Mo or W; $L_2 = CH_3SCH_2SCH_3$; R = CH_3), (M = Mo; L = CH_3CN; R = Cl), and (M = Mo; L = CH_3CN; R = Bu) [4–8] are known. The common feature of the reported structures [5,6] is a seven-coordinate environment in which a chlorine atom bridges the M–Sn bond (M = Mo or W) giving unusual pentacoordination around the tin. In contrast, the structure of the related complex $[Mo(CO)_2\{P(OMe)_3\}_3(SnCl_2Bu)Cl]$, which contains bulkier ligands than the other examples, shows the chlorine atom to be at a large distance from the tetrahedral tin atom, with a nearly linear Sn–Mo–Cl rearrangement [7].

The reactions which produce these compounds have been described as oxidative additions of the tin(IV) derivative to the starting Mo carbonyl complex. However, the formation of the trimetallic derivative $[(bipy)(CO)_3ClMo(\mu\text{-}SnCl_2)MoCl(CO)_3(bipy)]$ has been considered to be an insertion of an $Mo(CO)_3(bipy)$ fragment into the Sn–Cl bond of the starting $[MoCl(SnCl_3)(CO)_3(bipy)]$ [9]. We think that the same criterion could be used to explain the formation of all the above heterobimetallic compounds. Insertion of the 16-electron fragment, $Mo(CO)_3(CH_3CN)_2$, into the Sn–X bond of the haloorganotin derivative should be an appropriate way to produce new Mo–Sn systems.

We propose to investigate the requirements to produce heptacoordinate molybdenum compounds bonded to tin and bridged by chlorine. Following our previous work in which $RSnCl_3$ (R = Me or Ph) were allowed to react with $[(phen)\{P(4\text{-}XC_6H_4)_2\}Mo(CO)_3]$ derivatives [10], we studied reactions of $[Mo(CO)_3(CH_3CN)_3]$ with $SnRCl_3$ (R = Me or Ph). The different electronic and steric requirements of Me and Ph groups involved in the reactions should influence the production of a pentacoordinate tin environment as well as the stability of the heterobimetallic products.

2. Results and discussion

The new complexes $[Mo(SnRCl_2)(CH_3CN)_2(CO)_3Cl]$ [(1) R = C_6H_5, (2) R = CH_3] are yellow solids, light-

---

Correspondence to: Professor M. Cano.

0022-328X/93/$6.00

sensitive, air-unstable, but stable when stored under dinitrogen in the dark. They are soluble in the common solvents, but the solutions show slow changes at room temperature, to produce [Mo(CO)$_6$] and other decomposition products. This occurs in some cases even under di-nitrogen. Repeated attempts to obtain adequate crystals for crystal structure determination failed, and only decomposition products were recovered. The complexes were fully characterized by IR. ^{1}H and ^{13}C NMR (Table 1), UV-vis and Mössbauer spectroscopies. The compounds are non-conductors in acetone solution (10^{-3} M). The analytical data are consistent with the proposed formulations.

2.1. Characterization of the complexes

2.1.1. IR spectroscopy

The infrared spectra of the compounds [Mo(SnRCl$_2$)(CH$_3$CN)$_2$(CO)$_3$Cl] [(**1**) R = C$_6$H$_5$, (**2**) R = CH$_3$] in the solid state show two bands in the carbonyl stretching region at 1998vs, 1925sh–1904vs, and 2006vs, 1919sh–1898vs, respectively. The pattern of the bands, one sharp, and the other broad and split, suggests a *fac*-distribution of the three carbonyl groups [11]. These bands are shifted to higher frequencies compared to those of the parent compound [Mo(CH$_3$CN)$_3$(CO)$_3$] (1916 and 1797 cm^{-1}) [12], consistent with the increase of the formal oxidation state of molybdenum from 0 to II.

Two sharp bands appear in the 2300–2280 cm^{-1} region. The band at higher frequency is assigned to ν(CN) and the other one to a combination mode from δ_s(CH$_3$) and ν(C–C) [13]. Both bands are subject to Fermi resonance coupling so it was necessary to correct the observed values of these frequencies [14,15] (Table 1). Each band has a similar intensity, consistent with *cis* nitrile groups [15]. This is the main spectroscopic difference between the *cis* and *trans* nitrile isomers in related bis(nitrile) derivatives [15].

The IR spectra, in the ν(CO) region, of **1** and **2** in different solvents (Table 2) show two strong absorption bands, consistent with the presence of only one isomer. The second band is broad or split, depending on the solvent employed. O-donor solvents produce the largest shifts of ν(CO) values to lower frequencies with respect to those observed in CH$_3$CN solution.

TABLE 1. Selected nitrile ligand bands in the IR spectra of the compounds [Mo(SnRCl$_2$)(CH$_3$CN)$_2$(CO)$_3$Cl] [R = Ph (**1**), Me (**2**)]

1	**2**	Assignment
1362m	1366m	δ_s(CH$_3$)
939w	945w	ν(C–C)
2309s	2319s	ν(CN) [a]
2282s	2292s	
2290	2300	Corrected ν(CN) [14,15]

[a] Fermi resonance with δ_s(CH$_3$) + ν(C–C).

TABLE 2. Values of ν(CO) (cm^{-1}) of **1** and **2** in different solvents [a]

Solvent	**1**	**2**
Acetonitrile	2017vs, 1932sh, 1916vs	2014vs, 1930sh, 1919vs
Acetone	2007vs, 1921sh, 1902vs	1997vs, 1907sh, 1890vs
Dichloromethane	2017vs, 1935sh, 1920vs	2016vs, 1932sh, 1899vs
Ethanol	2005vs, 1920sh, 1903vs	2004vs, 1919sh, 1899vs
Chloroforme	2013s, 1915s,b	2012s, 1909s,b
Benzene	2009s, 1923s,b	2009s, 1925s,b
Toluene	2020s, 1927s,b	2020s, 1927s,b

[a] vs, very strong; s, strong; sh, shoulder; b, broad.

For non-isomeric forms of related seven-coordinate compounds, the position of the ν(CO) band of highest energy and the magnitude of the separation (Δ) of the two lower energy bands may be used to assign the geometry of the complex [16]. On this basis, and from our IR data (Table 2), a capped octahedral geometry seems reasonable.

2.1.2. ^{1}H and ^{13}C NMR spectroscopy

Table 3 summarizes the ^{1}H and ^{13}C NMR spectra and their assignments. Both compounds (**1** and **2**) show two ^{1}H NMR signals, at 2.63, 2.56 ppm and 2.63, 2.60 ppm, respectively, consistent with two different nitrile groups. In addition, in both complexes a signal is observed at 2.40 ppm, attributed to the protons of CH$_3$ groups of coordinated acetone.

In addition, the spectrum of **2** shows three signals at 1.5, 1.45 and 1.42 ppm, with their corresponding tin satellites, which are unequivocally assigned to different CH$_3$ groups bonded to tin.

TABLE 3. ^{1}H and ^{13}C NMR data (ppm) of **1** and **2**

		1	**2**
^{1}H NMR	δ(CH$_3$CN)	2.63 [a], 2.56	2.63 [a], 2.60
	δ(CH$_3$COCH$_3$)	2.40	2.40
	δ(CH$_3$Sn) [c]	–	1.5 [b], 1.45 [a], 1.42
^{13}C NMR	δ(CO)	197.71	199.91
	δ(C$_6$H$_5$)	148.43, 135.7 [d], 131.19, 129.56	–
	δ(–CN)	127.71, 117.68 [f]	127.27, 126.26, 117.68 [f]
	δ(CH$_3$Sn)	–	14.98 [e]
	δ(CH$_3$CN)	3.18, 3.01 [a], 1.1 [f]	3.19, 2.98 [a], 1.16 [f]

[a] Attributed to [Mo(SnRCl$_2$)(CH$_3$COCH$_3$)(CH$_3$CN)(CO)$_3$Cl]. [b] Attributed to [Mo(SnRCl$_2$)(CH$_3$COCH$_3$)$_2$(CO)$_3$Cl]. [c] $J(^{119}$Sn–CH$_3) = 73.7$ Hz, $J(^{117}$Sn–CH$_3) = 70.7$ Hz (1.5 ppm); $J(^{119}$Sn–CH$_3) = 75.2$ Hz, $J(^{117}$Sn–CH$_3) = 71.9$ Hz (1.45 ppm); $J(^{119}$Sn–CH$_3) = 76.1$ Hz, $J(^{117}$Sn–CH$_3) = 72.8$ Hz (1.42 ppm). [d] ^2J(Sn–C) = 61.4 Hz. [e] ^1J(Sn–C) = 291.7 Hz. [f] Attributed to free CH$_3$CN.

After 24 h, the intensity of the signals has decreased, especially those due to CH_3CN. The signals at 2.56 ppm (**1**) and 2.60 ppm (**2**) decrease *ca.* 70% and the signals at 2.63 ppm (**1** and **2**) *ca.* 40%. These observations are consistent with reactions in solution, possibly involving substitution of CH_3CN groups by solvent molecules, yielding $[Mo(SnRCl_2)(CH_3CN)(CH_3COCH_3)(CO)_3Cl]$.

This suggestion is also supported by the observation in the spectrum of **2** of signals at 1.42, 1.45, 1.50 ppm, the last of which is assigned to a new compound $[Mo(SnRCl_2)(CH_3COCH_3)_2(CO)_3Cl]$.

The ^{13}C NMR spectra show the presence of free acetonitrile [17], which is consistent with the substitution of this ligand by solvent to produce new species. The single signal observed at *ca.* 198 ppm is assigned to the carbonyl groups bonded to the molybdenum atom. This fact suggests an equivalence of the three carbonyl ligands, which is attributed to a fluxional process at room temperature [18]. The other assignments (Table 3) are also consistent with the above suggestions.

2.1.3. Mössbauer spectroscopy

The new heterobimetallic compounds $[Mo(SnRCl_2)(CH_3CN)_2(CO)_3Cl]$ [(**1**) $R = C_6H_5$, (**2**) $R = CH_3$] described must contain Mo–Sn and Mo–Cl bonds to achieve an 18-electron configuration around the heptacoordinate molybdenum. However, the crystal structure and the Mössbauer spectroscopy of the related compound $[Mo(SnCH_3Cl_2)(bipy)(CO)_3Cl]$ [5,19] indicated the presence of an additional interaction between the molybdenum and tin atoms through a bridged chloride which produced five-coordination at tin.

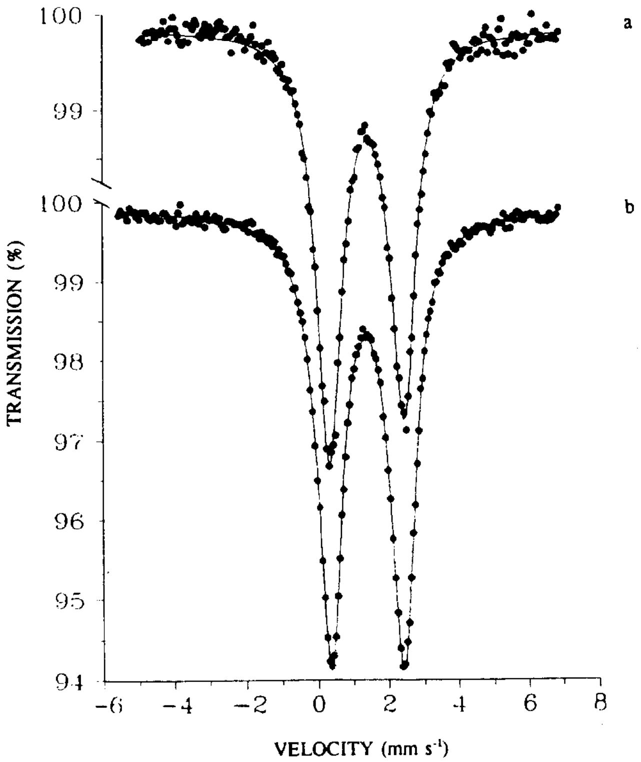


Fig. 1. Mössbauer spectra of $[Mo(SnC_6H_5Cl_2)(CH_3CN)_2(CO)_3Cl]$ (a) and $[Mo(SnCH_3Cl_2)(CH_3CN)_2(CO)_3Cl]$ (b) at 77 K.

A similar situation is suggested for our compounds. Figure 1 shows the Mössbauer spectra of **1** and **2**. The

TABLE 4. Heating of **1** and **2** in various solvents [a]

Compound	Solvent	Temperature (°C)	Time (h)	Atmosphere	Species observed
1	CH_2Cl_2	40	24	N_2	Starting compound
	$(CH_3)_2CO$	53	1–40	N_2	Starting compound + evolved species
	$(CH_3)_2CO$	53	50	N_2	Starting compound + evolved species + $[Mo(CO)_6]$
	$(CH_3)_2CO$	53	52	N_2	$[Mo(CO)_6]$
	C_6H_6	80	1	N_2	Starting compound
	C_6H_6	80	3	N_2	Starting compound + $[Mo(CO)_6]$
	C_6H_6	80	12	N_2	$[Mo(CO)_6]$
	$CH_3C_6H_5$	110	0.5	N_2	Starting compound + $[Mo(CO)_6]$
	$CH_3C_6H_5$	110	3	N_2	$[Mo(CO)_6]$
2	CH_2Cl_2	40	24	N_2	Starting compound
	$(CH_3)_2CO$	53	5	N_2	Starting compound + evolved species
	$(CH_3)_2CO$	53	48	N_2	Starting compound + evolved species + $[Mo(CO)_6]$
	$(CH_3)_2CO$	53	51	N_2	$[Mo(CO)_6]$
	C_6H_6	80	1	N_2	Starting compound + $[Mo(CO)_6]$
	C_6H_6	80	7	N_2	$[Mo(CO)_6]$
	C_6H_6	80	0.5	CO	Starting compound + $[Mo(CO)_6]$
	C_6H_6	80	1	CO	$[Mo(CO)_6]$

[a] IR spectra were monitored at hourly intervals.

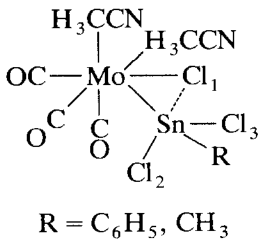


Fig. 2. Proposed structure for the complexes [Mo(SnRCl$_2$)(CH$_3$CN)$_2$(CO)$_3$Cl] [(1) R = C$_6$H$_5$, (2) R = CH$_3$].

isomer shifts (i.s.) in both cases are consistent with an oxidation state IV for tin. The i.s. and quadrupole splitting (q.s.) values (**1** i.s. = 1.44, q.s. = 2.08 mm s^{-1}; **2** i.s. = 1.41, q.s. = 2.04 mm s^{-1}) are smaller than the corresponding values for the related compound [Mo(SnCH$_3$Cl$_2$)(bipy)(CO)$_3$Cl] [19] (i.s. = 1.54, q.s. = 2.44 mm s^{-1}). The decrease in i.s. values implies a decrease in the electron density of the tin atom, suggesting five-coordination in the complexes **1** and **2**. It is also in agreement with the presence of a Mo–Sn $\cdots$ Cl unit in which a Mo–Sn bond bridged by a chloride atom is implicated, the Sn $\cdots$ Cl interaction being stronger than that observed in [Mo(SnCH$_3$Cl$_2$)(bipy)-(CO)$_3$Cl] [19]. Then, an environment around the tin atom like that represented in Fig. 2 is proposed for our complexes.

Both **1** and **2** have similar i.s. values, independent of R. This has two possible explanations. One is that the Mo–Sn $\cdots$ Cl bridge bond is weaker for complex **1** than for complex **2**. The other is that the greater s electron density on the tin in complex **2** due to the methyl is compensated for by a great electron delocalization through the Sn–L bond where L = Mo(CH$_3$CN)$_2$-(CO)$_3$Cl.

2.2. Changes of complexes in solution

We have carried out an IR study of the behaviour of complexes **1** and **2** in different solvents, at room and reflux temperature. The results are summarized in Table 4. The important observations are summarized below.

There is no detectable modification of the initial species in acetonitrile and dichloromethane solution even after several hours. However, in dichloromethane solution, there is a band assigned to [Mo(CO)$_6$], which increases in intensity with time. In acetone and ethanol solution, absorptions due to the initial species and new bands attributed to evolved products were observed. This was evident from zero time when acetone and a concentration of 0.045 M or less were used.

In both solvents, a band assigned to [Mo(CO)$_6$] was observed, but after different times, and in acetone at 0.01125 M after 48 h this was the only band observable.

The rate of decomposition and the formation of [Mo(CO)$_6$] increases with the temperature even under dinitrogen. Coordinating solvents give rise to intermediate species which appear to stabilise the initial products.

A scheme for the decomposition of the complexes is given in Fig. 3. The disproportionation of Mo^{II} to Mo^{III} derivatives and [Mo(CO)$_6$] has been already proposed for related complexes [20].

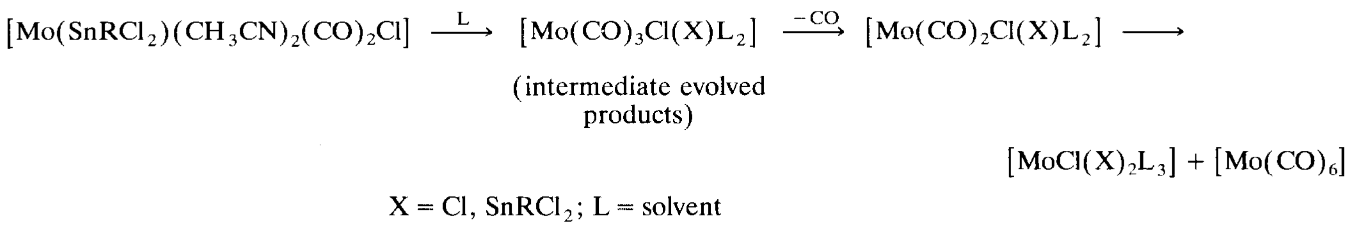
2.2.1. UV-vis spectroscopy

We could not use acetone solvent due to the range of its characteristic absorption. In EtOH, concentrations of 9×10^{-4} and 3×10^{-3} for **1** and **2**, respectively, were required to observe spectral changes.

The conversion of the parent compounds [λ_{max} = 386 nm (**1**) and 375 nm (**2**)] to an intermediate species [λ_{max} = 404 nm (**1**) and 401 nm (**2**)] takes place in 33 and 8 min for complexes **1** and **2**, respectively. Isosbestic points appear at 393 nm (**1**) and 375 nm (**2**). After 24 h, a new absorption was observed at 290 nm, attributed to [Mo(CO)$_6$] [21]. The isosbestic point could not be observed when lower concentrations were employed, consistent with the presence of the new species from the beginning of the reaction. Concentration appears to be a determining factor in the above process.

In CH$_2$Cl$_2$ solution, independent of the concentrations employed, the complexes show only an absorption at 377 nm of the initial species, which decreases at the same time as the band at 290 nm, characteristic of [Mo(CO)$_6$] [21], increases.

All the above results show that the complexes generate [Mo(CO)$_6$] in solution, but the detailed mechanism depends on solvent and concentration.



$$[\mathrm{Mo(SnRCl_2)(CH_3CN)_2(CO)_2Cl}] \xrightarrow{L} \underset{\text{(intermediate evolved products)}}{[\mathrm{Mo(CO)_3Cl(X)L_2}]} \xrightarrow{-CO} [\mathrm{Mo(CO)_2Cl(X)L_2}] \longrightarrow [\mathrm{MoCl(X)_2L_3}] + [\mathrm{Mo(CO)_6}]$$

$\mathrm{X = Cl, SnRCl_2;\ L = solvent}$

Fig. 3. Possible route of decomposition of the complexes [Mo(SnRCl$_2$)(CH$_3$CN)$_2$(CO)$_3$Cl] in solution.

. Concluding remarks

Two heptacoordinate MoII complexes containing hree *facial* CO groups, two *cis* CH_3CN groups and he last two positions occupied by a Cl and $SnRCl_2$ R = CH_3 or C_6H_5) were obtained (Fig. 2). A capped octahedral geometry is proposed in which there is a Mo–Sn bond bridged by a chlorine. The complexes decompose in solution to produce $[Mo(CO)_6]$. When donor solvents are used, the decomposition occurs hrough intermediate species produced by substitution of CH_3CN by solvent molecules. $[Mo(SnC_6H_5Cl_2)$-$CH_3CN)_2(CO)_3Cl]$ (**1**) is more stable in solution than $Mo(SnCH_3Cl_2)(CH_3CN)_2(CO)_3Cl]$ (**2**). The IR and Mössbauer spectra of **1** and **2** reflect the different natures of CH_3 and C_6H_5.

. Experimental details

All reactions were carried out under dinitrogen by tandard Schlenk line techniques. Elemental analyses or carbon, hydrogen and nitrogen were carried out by he Microanalytical Service, Universidad Autónoma de Madrid.

IR spectra were recorded on a Nicolet 5DX FT-IR pectrometer. ^1H and ^{13}C spectra were recorded on a Varian XL-300 spectrometer (shifts are relative to inernal tetramethylsilane). Electronic spectra were ecorded on a Milton Roy Spectronic 3000 Array specrophotometer. 119-Tin Mössbauer spectra were obained with a constant-acceleration Mössbauer specrometer [22]. A standard source of $Ca^{119}SnO_3$ was used at room temperature in transmission geometry, and the polycrystalline samples were cooled to 77 K in a liquid nitrogen cryostat. Isomer shifts are relative to $BaSnO_3$ at room temperature, and the estimated error s ±0.05 mm s^{-1}.

.1. *Synthesis of* $[Mo(SnC_6H_5Cl_2)(CH_3CN)_2(CO)_3Cl]$ 1)

A suspension of $[Mo(CO)_6]$ (2.5 g, 94 mmol) in degassed acetonitrile (75 ml) was heated under reflux under dinitrogen for 14 h to give a yellow solution of $Mo(CH_3CN)_3(CO)_3]$ [23]. Addition of $SnC_6H_5Cl_3$ (2.86 g, 94 mmol) and stirring at room temperature for 2 h gave an orange-red solution. After removal of the solvent, the residue was recrystallized from CH_3-CN/Et_2O to afford yellow powder (**1**) (4.54 g, 85%). Anal. Found: C, 27.29; H, 190; N, 4.90. $C_{13}H_{11}Cl_3MoN_2O_3Sn$ calc.: C, 27.67; H, 1.96; N, 4.96% IR (Nujol): 1998vs; 1925sh; 1904vs [ν(CO)] cm^{-1}. Mössbauer (77 K): i.s. = 1.44, q.s. = 2.08 mm s^{-1}.

Complex **2** was prepared similarly. $[Mo(SnCH_3Cl_2)$-$(CH_3CN)_2(CO)_3Cl]$ (**2**): yellow powder (77%). Anal. Found: C, 19.00; H, 1.79; N, 5.68. $C_8H_9Cl_3MoN_2O_3Sn$ calc.: C, 19.13; H, 1.81; N, 5.58%. IR (Nujol): 2006vs; 1919sh; 1898vs [ν(CO)] cm^{-1}. Mössbauer (77 K): i.s. = 1.41, q.s. = 2.04 mm s^{-1}.

Acknowledgments

We thank Dr. D. Tudela for his help in the interpretation of Mössbauer spectra. Financial support for this work from the Comisión Asesora de Investigación Científica y Técnica (CAICYT) is gratefully acknowledged (Projects No. 367/84 and PB87-0125).

References

1 L. Bencze and A. Krant-Vass, *J. Mol. Catal.*, *28* (1985) 369.
2 L. Bencze, A. Krant-Vass and L. Prókai, *J. Chem. Soc., Chem. Commun.*, (1985) 911.
3 H.X. Zhang, F. Guibé and G. Balavoine, *J. Org. Chem.*, *55* (1990) 1857.
4 R. Kummer and W.A.G. Graham, *Inorg. Chem.*, *7* (1968) 310.
5 M. Elder and D. Hall, *Inorg. Chem.*, *8* (1969) 1268.
6 R.A. Anderson and F.W.B. Einstein, *Acta Crystallogr. Sect. B*, *32* (1976) 966.
7 D. Miguel, J.A. Pérez-Martínez, V. Riera and S. García-Aranda, *Polyhedron*, *10* (1991) 1717.
8 P.K. Baker and A. Bury, *J. Organomet. Chem.*, *359* (1989) 189.
9 J. Granifo, *Polyhedron*, *9* (1990) 1187.
10 M. Cano and M. Panizo, *Polyhedron*, *9* (1990) 2863.
11 E.E. Isaacs and W.A.G. Graham, *Inorg. Chem.*, *14* (1975) 2560.
12 B.L. Ross, J.G. Grasselli, W.M. Ritchey and H.D. Kaesz, *Inorg. Chem.*, *2* (1963) 1023.
13 J.B. Milne, *Can. J. Chem.*, *48* (1970) 75.
14 B.N. Storhoff and H.C. Lewis, Jr., *Coord. Chem. Rev.*, *23* (1977) 1.
15 Y. Kawano, Y. Hasse and O. Sala, *J. Mol. Struct.*, *30* (1976) 45.
16 T.E. Reed and D.G. Hendricker, *Chubu Kojyo Baigaku Kijo A*, (1978) 175.
17 E. Pretsch, T. Clerc, J. Seibl and W. Simon, *Tablas para la elucidación estructural de los compuestos orgánicos*, Alhambra, Madrid, 1985, p. C150.
18 M.G.B. Drew, P.K. Baker, E.M. Armstrong and S.G. Fraser, *Polyhedron*, *7* (1988) 245.
19 W.R. Cullen, R.K. Pomeroy, J.R. Sams and T.B. Tsin, *J. Chem. Soc., Dalton Trans.*, (1975) 1216.
20 D. Westland and N. Muriithi, *Inorg. Chem.*, *11* (1972) 2971.
21 H.B. Gray and N.A. Beach, *J. Am. Chem. Soc.*, *85* (1963) 3533.
22 J.D. Tornero, Ph.D., Autónoma University of Madrid, 1980.
23 D.P. Tate, W.R. Knipple and J.M. Augl, *Inorg. Chem.*, *1* (1962) 433.