Synthesis and characterization of copper and manganese complexes of monodentate functionalized isocyanide: trimethylsilylmethylisocyanide and *p*-tolylsulfonylmethylisocyanide

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Abstract

Reaction of excess $CNCH_2SiMe_3$(L) with $CuX_2 \cdot nH_2O$ ($X = NO_3^-$, $n = 3$; ClO_4^-, $n = 6$) in THF gives the Cu^I complexes $[CuL_4]NO_3$ (**1**) and $[CuL_4]ClO_4$ (**2**). When CuCN is used as starting material, complex **3**, $Cu(L_3)CN$, $C_4H_{10}O \cdot 3H_2O$, is obtained. Immediate reduction occurs with $AgNO_3$ precipitating metallic Ag. Reactions with $MnCl_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ in THF produce two new compounds which analyze as $MnL_4Cl_2 \cdot 4H_2O$ (**6**) and $MnL_2(NO_3)_2 \cdot H_2O$ (**7**). When excess *p*-tolylsulfonylmethylisocyanide (L′) is reacted with $Cu(NO_3)_2$, the mixed-valence Cu^I–Cu^{II} complex $Cu_2L'_6(NO_3)_3$ (**5**) is precipitated, while using CuCN gives the Cu^I dimer $Cu_2L'_4(CN)_2$ (**4**). In analogous conditions the manganese complex $MnL'_2(NO_3)_2 \cdot C_3H_6O \cdot 3H_2O$ (**8**) is precipitated. All these complexes have been isolated, characterized by IR, NMR for diamagnetic species, magnetic susceptibilities, EPR measurements and electrochemical analyses. Influence of the two substituents is discussed.

Introduction

Isocyanides have attracted a great deal of attention as ligands toward metal centers [1]. Because of their electronic properties (strong σ-donor and π-acceptor) and low steric requirement (linear molecule) [2], they have been used to mimic CO reactivity [3, 4]. Although they are able to react with metals in high oxidation states, their reducing properties make them most of the time more suitable to stabilize metals in low oxidation states [5].

Their metal complexes have been used for energy storage, chemical syntheses and catalysis [6]. Monodentate isocyanides have recently been examined in relation to their ability to give stable Tc^I complexes with radiopharmaceutical applications. In this field, the MIBI complex, $[Tc(CNR)_6]^+$ (R = 2-methoxyisobutylisocyanide), is commercially used as a myocardic agent [7]. Consequently, many isocyanide molecules CNR have been synthesized, R covering a wide range of substituents [8]. A way of introducing isocyanide into the Tc species, which prevents ligand decomposition, is to use isocyanide transfer from first row metal complexes as precursors [9]. This implies the knowledge of such species.

It is apparent that the reaction of isocyanides bearing silicium SiR_3 or $SO_2C_7H_7$ substituent with metal salts has not yet been reported. In the present study, we describe the reaction of excess of trimethylsilylmethylisocyanide $CNCH_2SiMe_3$ and *p*-tolylsulfonylmethylisocyanide, $CNCH_2SO_2C_7H_7$, with the first row metal salts MX_2 ($M = Cu^{II}$ and Mn^{II}; $X = NO_3^-$, ClO_4^-, Cl^-). These metals were selected because they adopt different coordination geometries, show different abilities to participate in redox processes and give products with variable solubilities in polar and non-polar solvents. Moreover, if $CNCH_2SiMe_3$ is monodentate, $CNCH_2SO_2C_7H_7$ possesses two coordination sites: the isocyanide carbon atom and the SO_2 function. Both could be involved in the coordination. Many copper(I) and (II) [10] and manganese(I) [11, 12] complexes with isocyanide ligands are known, but manganese(II) species are not so common [13]. They have been synthesized by oxidation of the appropriate Mn^I complex, although a recent report related their formation by reaction of CN^tBu on the manganese(II) compound $MnI_2(PPh_3)_2$ [14].

Experimental

Reactions

All reactions were carried out at room temperature under N_2. The solvents were distilled immediately before use.

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Trimethylsilylmethylisocyanide was synthesized following the literature method [15] and kept at −25 °C to prevent polymerization. It is a yellow liquid ($d = 0.8$ g/cm^3). *p*-Tolylsulfonylmethylisocyanide (Aldrich) is a beige, moisture sensitive, powder which must be kept at −18 °C. The metal salts: $Cu(ClO_4)_2 \cdot 6H_2O$, CuCN, $MnCl_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$ (Aldrich) and $Cu(NO_3)_2 \cdot 3H_2O$ (Prolabo) were used as received when reacted with $CNCH_2SiMe_3$. They were dehydrated by reaction with dimethoxypropane and dried *in vacuo* when $CNCH_2SO_2C_7H_7$ was used.

C, H, N, S elemental analyses were performed by the Service de Microanalyse du Laboratoire de Chimie de Coordination du C.N.R.S., Toulouse and Cu, Mn, Si, Cl, O by the Service Central de Microanalyse du C.N.R.S., Lyon, France.

[Cu(CNCH₂SiMe₃)₄]NO₃ (1)

Trimethylsilylmethylisocyanide (2.51 ml, 24.84 mmol) was added slowly to a blue THF solution (40 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (1 g, 4.14 mmol). The solution was stirred for 6 h whereupon it turned green, and was then concentrated to 10 ml. A white powder precipitated immediately, which was filtered, washed with diethyl ether and dried *in vacuo*. A second crop of product was obtained by addition of diethyl ether. Yield 85%. *Anal.* Calc. for $CuC_{20}H_{44}N_5O_3Si_4$: C, 41.52; H, 7.66; N, 12.10. Found: C, 41.57; H, 7.89; N, 12.32%.

[Cu(CNCH₂SiMe₃)₄]ClO₄ (2)

To a stirred solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.5 g, 1.35 mmol) in THF (50 ml) was added trimethylsilylmethylisocyanide (1.14 ml, 8.1 mmol), whereupon the solution turned yellow–green. After 12 h of stirring, the solution was concentrated at room temperature. Addition of 20 ml of diethyl ether precipitated a beige powder which was filtered, washed with diethyl ether and dried *in vacuo*. Yield 83%. *Anal.* Calc. for $CuC_{20}H_{44}N_4O_4Si_4Cl$: C, 39.0; H, 7.20; N, 9.10. Found: C, 38.53; H, 7.40; N, 8.86%.

Cu(CNCH₂SiMe₃)₃(CN)·C₄H₁₀O·3H₂O (3)

To 0.25 g (2.80 mmol) of CuCN in suspension in 50 ml of THF were added slowly 1.18 ml of trimethylsilylmethylisocyanide. The mixture was stirred for 24 h until the copper compound dissolved completely. The solution, which had turned yellow–orange, was then concentrated to 10 ml *in vacuo*. Addition of 30 ml of diethyl ether precipitated a white powder which was filtered, washed several times with diethyl ether and dried *in vacuo*. The anhydrous solid reacted with water in the air giving the trihydrate **3** which is stable. Yield 80%. *Anal.* Calc. for $CuC_{20}H_{49}N_4O_4Si_3$: C, 43.09; H, 8.86; N, 10.05; Si, 15.11; Cu, 11.4. Found: C, 43.09; H, 8.63; N, 9.92; Si, 15.65; Cu, 11.87%.

Cu₂(CNCH₂SO₂C₇H₇)₄(CN)₂ (4)

Tosylmethylisocyanide (1.41 g, 7.22 mmol) dissolved in dichloromethane (20 ml) was added through a cannula to a stirred THF suspension (20 ml) of CuCN (0.16 g, 1.79 mmol). The mixture was stirred for 24 h until the copper salt dissolved giving an orange solution. Concentration of the solution to 10 ml produced a white precipitate which was filtered, washed with diethyl ether and dried *in vacuo*. Yield 65%. *Anal.* Calc. for $Cu_2C_{38}H_{36}N_6O_8S_4$: C, 47.54; H, 3.78; N, 8.75; S, 13.36; Cu, 13.24. Found: C, 47.82; H, 3.82; N, 8.87; S, 12.62; Cu, 13.03%.

Cu₂(CNCH₂SO₂C₇H₇)₆(NO₃)₃ (5)

To 0.62 mmol (0.12 g) of $Cu(NO_3)_2$ in THF (20 ml) were added slowly through a cannula 3.17 mmol (0.62 g) of tosylmethylisocyanide in dichloromethane (20 ml). The solution turned green. It was stirred for 6 h then concentrated to produce a green powder, which was filtrated, washed with 20 ml of diethyl ether and dried *in vacuo*. Yield 70%. *Anal.* Calc. for $Cu_2C_{54}H_{54}N_9O_{21}S_6$: C, 43.69; H, 3.67, N, 8.49; S, 12.96; Cu, 8.56. Found: C, 43.95; H, 4.13; N, 6.93; S, 11.88; Cu, 9.14%.

Mn(CNCH₂SiMe₃)₄Cl₂·4H₂O (6)

To 0.5 g (2.52 mmol) of $MnCl_2 \cdot 4H_2O$ suspended in 40 ml of THF were added 2.14 ml of trimethylsilylmethylisocyanide. The mixture was stirred for 18 h until the manganese salt dissolved giving a red–brown and clear solution. Evaporation of THF and ligand in excess *in vacuo* gave a brown oil. This oil was washed several times with large amounts of diethyl ether until a brown hygroscopic powder precipitated, which was dried *in vacuo*. Yield 65%. *Anal.* Calc. for $MnC_{20}Cl_2H_{52}Si_4N_4O_4$: C, 36.91; H, 8.05; N, 8.61; Si, 17.26; Mn, 8.44. Found: C, 36.81; H, 7.90; N, 8.70; Si, 17.60; Mn, 8.30%.

Mn(CNCH₂SiMe₃)₂(NO₃)₂·H₂O (7)

By a similar procedure, excess trimethylsilylmethylisocyanide (0.98 ml, 6.97 mmol) was added to a stirred methanol solution (40 ml) of $Mn(NO_3)_2 \cdot 6H_2O$ (0.5 g, 1.74 mmol). A brown oil was obtained after 18 h of stirring. Evaporation of the solvent and workup produced **5** as a brown hygroscopic powder. Yield 62%. *Anal.* Calc. for $MnC_{10}H_{24}N_4O_7Si_2$: C, 28.37; H, 5.71; N, 13.23; Si, 13.27; Mn, 12.97. Found: C, 28.04; H, 5.90; N, 11.10; Si, 13.83; Mn, 13.08%.

Mn(CNCH₂SO₂C₇H₇)₂(NO₃)₂·C₃H₆O·3H₂O (8)

This hygroscopic compound was obtained from dehydrated $Mn(NO_3)_2$ (0.4 g, 2.23 mmol) and $CNCH_2SO_2C_7H_7$ (2.61 g, 13.41 mmol) following the same procedure. Yield 55%. *Anal.* Calc. for $MnC_{18}H_{26}O_{14}N_4S_2$: C, 33.7; H, 4.09; N, 8.73; S, 10; Mn, 8.56. Found: C, 33.69; H, 4.33; N, 7.81; S, 8.93; Mn, 8.52%.

Physical measurements

IR spectra were recorded as Nujol mulls on a Perkin-Elmer 398 spectrophotometer. ^1H NMR spectra were recorded on Bruker AC 80 or AC 200 spectrophotometers. EPR spectra were measured on a Bruker ER 200 TT spectrophotometer operating at X-band frequency between 95 and 300 K. Magnetic susceptibilities were determined by the Faraday method, using a Cahn microbalance coupled with a Drusch electromagnet. Measurements were performed between 20 and 320 K. $HgCo(NCS)_4$ was used as standard ($Xg = 16.44\ 10^{-6}$ cgs emu). The experimental values were corrected for the diamagnetism of the ligands [16]. Mass spectra were recorded on a NERMAG R 1010 spectrometer (GC/MS). The samples were chemically ionized with NH_3 as gas vector.

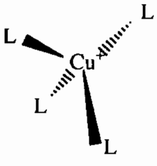
Electrochemical measurements were carried out with a home-made potentiostat controlled by an Apple IIe microcomputer [17]. The electrochemical cell was a conventional three electrodes system: working electrode, Pt(EDI Tacusscl, area 3.14 mm^2) or glassy carbon electrode (diameter 3 mm; area 7.06 mm^2); counter electrode, Pt wire; reference electrode, SCE separated from the solution by a fritted glassy junction. The supporting electrolyte Bu_4NPF_6 (Fluka, electrochemical grade) or $Bu_4N(ClO_4)$ (prepared from Bu_4NOH and $HClO_4$ and recrystallized from methanol) and the solvents, MeCN (SDS for ADN synthesis) and DMSO (Merck Analytical Grade), were used without any further purification.

Results

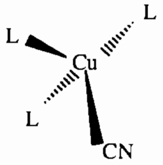
$CNCH_2SiMe_3$

Reactions of $CNCH_2SiMe_3$ with $AgNO_3$, $CuX_2 \cdot nH_2O$ ($X = NO_3$, $n = 3$; $X = ClO_4$, $n = 6$; $X = CN$, $n = 0$) and $MnX_2 \cdot 6H_2O$ salts ($X = NO_3$, Cl) were found to be dependent on the metal.

When employing $AgNO_3$, immediate reduction of Ag^+ occurred with precipitation of an Ag mirror. With copper(II) salts, complete reduction into the copper(I) analogs was observed. The two copper(I) compounds $[Cu(CNCH_2SiMe_3)_4]NO_3$ (**1**) and $[Cu(CNCH_2SiMe_3)_4]ClO_4$ (**2**) were quantitatively obtained as diamagnetic white powders when excess isocyanide was allowed to react with one mole of $CuX_2 \cdot nH_2O$. They are soluble in polar solvents and in CH_2Cl_2. Recrystallization of **1** in CH_2Cl_2/ether gave single crystals but not good enough for X-ray determination. They show a strong $\nu(CN)$ stretch at 2185 cm^{-1} in **1** and 2183 cm^{-1} in **2**, shifted to higher frequency by coordination from that of free ligand (2134 cm^{-1}) as expected for M–C σ bonding. This agrees with the ^1H NMR data which present for both compounds two singlets at 0.20 ppm for $SiMe_3$ and 3.0 ppm for the methylene group, slightly shifted to lower field when compared to the corresponding values (0.177 and 2.87 ppm) of the free ligand. Mass spectroscopic values of **1** indicate the presence of $M^{+\circ}$ at 515, in agreement with a monomeric species. Thus, all these data are consistent with the formation of tetrahedral Cu^I cations **A** since this geometry, common for d^{10} Cu^I complexes, has been structurally characterized for $[Cu(CNMe)_4]^+$.



A (**1**; **2**)



B (**3**)

Reaction of copper(I) cyanide CuCN with excess $CNCH_2SiMe_3$ at r.t. for 24 h in THF gave **3** as a white powder which analyzed as $Cu(CNCH_2SiMe_3)_3CN \cdot C_4H_{10}O \cdot 3H_2O$. The compound which first crystallized as the ether solvate, was hygroscopic and in air turned immediately into its trihydrate which was stable, easy to handle and gave reproducible microanalyzes. The presence of ether was deduced from the ^1H NMR which showed the two characteristic multiplets, a triplet at 1.35 ppm and a quadruplet at 3.07 ppm. The broad and strong $\nu(CN)$ band corresponding to the isocyanide stretch is present at 2150 cm^{-1} and the shoulder at 2171 cm^{-1} attributed to the cyanide vibration. **3** is thus best represented as a tetrahedral Cu^I species **B** the copper atom being bonded to three $CNCH_2SiMe_3$ ligands and one CN group, a structure which has already been reported for $Cu(CN)(CNR)_3$ ($R = C_2H_5$, C_5H_{11}) [18], ($R = C_4H_9$) [19], ($R = C_6H_5$) [20].

Interestingly, no manganese(II) reduction was observed. The two hygroscopic light brown manganese(II) compounds which analyzed as $Mn(CNCH_2SiMe_3)_4Cl_2 \cdot 4H_2O$ (**6**) and $Mn(CNCH_2SiMe_3)_2(NO_3)_2 \cdot H_2O$ (**7**) were obtained in high yield when excess $CNCH_2SiMe_3$ was added to $MnCl_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ in THF. They are soluble in acetone, dichloromethane, THF, acetonitrile and ethanol. **6** decomposes slowly in solution, losing isocyanide and producing $MnCl_2$ which was difficult to eliminate completely from the recrystallized solid and is responsible for the magnetic moment value of 6.52 BM, higher than the spin only value. The magnetic moment is $\mu_{eff} = 5.81$ BM for **7**. The EPR data for **6** and **7** listed in Table 1, were determined in acetone solutions. They indicate d^5 high-spin Mn^{2+} species in $^6A_{1g}$ ground state. Both complexes have equivalent isocyanide ligands as indicated by the pres-

TABLE 1. IR and magnetic data for the complexes

Compound	$\nu(C\equiv N)^a$ (cm^{-1})	$\mu_{eff}{}^b$ (BM)	EPR^c
$CNCH_2SiMe_3$ (L)	2134		
$CNCH_2SO_2C_7H_7$ (L′)	2145		
$[Cu(CNCH_2SiMe_3)_4]NO_3$ (**1**)	2185		
$[Cu(CNCH_2SiMe_3)_4]ClO_4$ (**2**)	2183		
$Cu(CNCH_2SiMe_3)_3CN\cdot C_4H_{10}O\cdot 3H_2O$ (**3**)	2150		
$Cu_2[CNCH_2SO_2C_7H_7]_4(CN)_2$ (**4**)	2165		
$Cu_2[CNCH_2SO_2C_7H_7]_6(NO_3)_3$ (**5**)	2190	1.3	$g_{\parallel}=2.4235$ ($A_{\parallel}=120$ G) $g_{\perp}=2.0887$
$Mn(CNCH_2SiMe_3)_4Cl_2\cdot 4H_2O$ (**6**)	2110	6.5	$\langle g\rangle$ 1.9875 $A=40$ G
$Mn(CNCH_2SiMe_3)_2(NO_3)_2\cdot H_2O$ (**7**)	2219	5.8	$\langle g\rangle=2.0066$ $A=70$ G
$Mn[CNCH_2SO_2C_7H_7]_2(NO_3)_2\cdot C_3H_6O\cdot 3H_2O$ (**8**)	2147	6.0	$\langle g\rangle=2.0047$ $A=63$ G

^{a}In the solid state as nujol mulls. ^{b}293 K. ^{c}In acetone solution at 90 K ($c=10^{-3}$ mol/l).

ence of only one ν(CN) stretch. Their values are significantly different: 2110 cm^{-1} for **6**, i.e. at lower field than the free ligand and 2219 cm^{-1} for **7**, i.e. at higher field. Such a large range of energies has already been observed from the ν(CN) stretch in the manganese–isocyanide complexes [13]. The number of $CNCH_2SiMe_3$ per metal, the absence of uncoordinated CN groups deduced from the IR spectra and X-ray data on Mn^{II}–CNR complexes suggest as the most probable a d^5 Mn^{2+} center surrounded by a tetrahedron of ligands, i.e. for **6**: 4-CNR and for **7**: 2-CNR and NO_3^-. In agreement with this is the conductivity value for **6** in methanol ($c=10^{-3}$ m l^{-1}) $\Lambda=277$ Ω^{-1} cm^2 mol^{-2} which shows the presence of a 2/1 electrolyte [21]. Many examples of metal coordinated NO_3 ligands have been reported indicating that in principle the coordination mode could be deduced from the IR data [22]. However, this is not possible here because of the superposition of ligand-skeleton vibrations.

$CNCH_2SiMe_3$ does not react with ZnX_2 salts ($X=Cl^-$, NO_3^-, $CF_3SO_3^-$) which is not unusual.

In order to get a deeper insight into the properties of this silyl substituted isocyanide, we have carried out experimental studies on the electrochemical properties of the ligand and of complexes **1**, **2** and **6**.

The voltammogram of $CNCH_2SiMe_3$, at a Pt electrode, presents only a quasi-irreversible reductive process at -1.16 V. A glassy carbon working electrode is needed to reach the oxidation wave at 2.02 V which results from an irreversible electronic transfer involving approximately two electrons*. Under the same experimental conditions, ^{t}BuNC does not exhibit any oxidation wave, which confirms that silyl substitution generally lowers the oxidation potential of a molecule [23].

Yet, no reversible couples were observed for the copper and manganese complexes which indicates participation of the ligand in the process. Cyclic voltammetry for **2**, in MeCN, at Pt electrode, shows two irreversible redox couples Cu^I/Cu^0 and Cu^I/Cu^{II}. The *i*/*E* curve of Cu^I/Cu^0 indicates the reduction of the ligand and the deposition of Cu^0 at -0.97 V. Redissolution of Cu^0 is not observed at -0.25 V as expected for Cu^0/Cu^{2+} (*vide infra*) but at -0.54 V which indicates formation of $[Cu^I(CNR)_x]^+$ species (for $v=0.1$ V/s). The *i*/*E* curve of Cu^I/Cu^{II} presents the shape of an irreversible process with $E_p\sim 1.28$ V at $v=0.1$ V/s. Surprisingly, the voltammogram of complex **1** shows no oxidation peak at Pt electrode and the use of a glassy carbon electrode is necessary to get the oxidation wave. Its *i*/*E* curve presents the pattern of an irreversible oxidative process at 2.07 V for $v=0.1$ V/s. Thus change of ClO_4^- by NO_3^- causes an important anodic shift in potential. Such shifts have already been observed for perchlorate complexes and attributed to coordination of ClO_4^- to the metal center. By comparison, NO_3^- acts here as a stronger ligand.

Cyclic voltammetry for the Mn complex **6**, on the other hand, shows an irreversible reduction wave Mn^{II}/Mn^I, at -1.04 V and a quasi reversible oxidation wave Mn^{II}/Mn^{III} at 1.18 V, implicating the transfer of one electron [24]. When the potential scan speed is increased, the peak ratio $R_{I_p}=I_{p\,\mathrm{backward}}/I_{p\,\mathrm{forward}}$ for the oxidation increases as for an EC scheme. However, the Mn^{III} is unstable, with a calculated half-life time of about 1 ms. Under stationary conditions, no diffusion

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*The experimental parameters are: $c(L)=2.8\times 10^{-3}$ mol/l; $E_{p\,ox}=2.018$ V ($v=0.1$ V/s); $I_p=74$ μA; $E_{1/2}=-2.12$ V ($\omega=1000$ t/min); $I_D=127$ μA ($\omega=1000$ t/min).

wave is observed because of the passivation of the electrode.

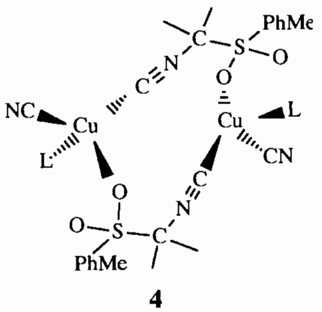
$CNCH_2SO_2C_7H_7$

Interestingly, a green slightly hygroscopic mixed-valence Cu^{II}–Cu^{I} complex which analyses as $Cu_2\{CNCH_2SO_2C_7H_7\}_6(NO_3)_3$ (**5**) precipitated in good yield when excess $CNCH_2SO_2C_7H_7$ was reacted with $Cu(NO_3)_2 \cdot 6H_2O$ in THF at r.t. **5** is soluble in THF, acetone, acetonitrile and ethanol but decomposes slowly in chlorinated solvents. Thus, the tosylisocyanide does not induce complete Cu^{II} reduction at room temperature.

Using identical conditions, the copper(I) complex $[Cu(CNCH_2SO_2C_7H_7)_2(CN)]_2$ (**4**) was obtained when CuCN was used as the starting compound. **4** is soluble in DMSO only, which is indicative of an oligomeric structure. Such a species has already been reported for CNPh [19].

Both complexes present only one ν(CN) vibration at 2165 cm^{-1} for **4** and 2187 cm^{-1} for **5**. They are shifted to higher energy upon complexation as expected (free ligand: 2145 cm^{-1}). The obtention of a higher value for **5** is consistent with the decrease of ν(CN) in the order $\nu(Cu^{I}) < \nu(Cu^{II}\text{–}Cu^{I}) < \nu Cu^{II})$ in agreement with the increased back-bonding from filled copper d orbitals into the NC π^* system [25]. Perturbation of the SO_2 function on coordination is deduced from the IR spectrum, which shows a high energy shift of the $\nu(SO_2)$ at 1031–1007 cm^{-1} compared to 970–935 cm^{-1} in the free ligand.

4 is diamagnetic as expected for Cu^{I} complexes, but **5** presents a low magnetic moment of 1.3 BM in the solid state at r.t. Presence of Cu^{I} centers in the ratio $Cu^{I}/Cu^{II} = 1/1$ may explain this low value since the EPR spectrum in acetone at 90 K shows the classical feature of magnetically diluted Cu^{II} centers in a tetrahedral environment ($A_{\parallel} = 120$ G) (Table 1). Interestingly, we have previously reported mixed-valence Cu^{II}–Cu^{I} complexes (with a ratio 1/1) with diisocyanides (diisocyanohexane and diisocyanoethane) [24]. Their IR, magnetic moment and EPR data are in excellent agreement with the values obtained here and confirm that **5** is probably a mixed-valence complex of type I, that is without magnetic interaction between the Cu^{II} atoms.



4

The probable dimeric nature of **4** is deduced from IR which shows a lower energy shift of the vibration corresponding to the SO_2 group, which appears at 909 and 897 cm^{-1} consistent with O-coordination [26].

The light brown compound which analyzes as $Mn(CNCH_2SO_2C_7H_7)_2(NO_3)_2 \cdot (Me_2CO) \cdot 3H_2O$ (**8**) was obtained in good yield when excess ligand was added to dehydrated $Mn(NO_3)_2 \cdot H_2O$. Surprisingly, the IR spectrum shows only one broad ν(CN) band at 2147 cm^{-1}, i.e. in the same range as for the free ligand and no shift of the $\nu(SO_2)$ substituent. The presence of acetone is deduced from the IR vibrations at 3375, 1705 and 900 cm^{-1}. The characterization of **8** as a tetrahedral d^5 high-spin Mn^{2+} complex is confirmed by the magnetic moment value of $\mu_{eff} = 6$ BM (solid, r.t.) and the EPR spectrum, typical of magnetically dilute Mn^{2+} centers, which gives a $\langle g \rangle$ value of 2.0047 at 90 K in acetone ($A = 63$ G). The coordination sphere including only two RNC groups for Mn^{2+} must be completed by NO_3 oxygen or water. Such a Mn^{2+} species $Mn(TMB)(CF_3SO_3)_2 \cdot 2H_2O$ has been precedently synthesized with TMB ligand (TMB = 2,5-dimethyl-2,5-diisocyanohexane).

$CNCH_2SO_2C_7H_7$ is non-electroactive at a Pt electrode, while on a Hg electrode it can be reduced to alkylisocyanide and thus detosylated through a 2e pathway [27]. At a glassy carbon electrode, reduction of the copper leads to the formation of Cu^0. The detosylation is ruled out because experimentally the reduction process Cu^+/Cu^0 requires $1e^-$ and not $3e^-$ as would be necessary for detosylation plus reduction. The irreversible oxidation wave is observed at 2.01 V, slightly lower than for the $SiMe_3$ analog. Only one electron is implicated in this process*.

Cyclic voltammetry for the Cu complex **5** shows, at platinum electrode, a reduction process at −1.47 V for $v = 0.1$ V/s, associated with Cu^0 deposit. This reduction shows on the reverse scan an oxidation step at −0.27 V, characteristic of oxidation of the Cu^0 deposit into Cu^{2+}. No oxidation process Cu^{I}/Cu^{II} is observed.

Due to the lack of solubility of complex **4** in MeCN, the electrochemical measurements were then carried out in DMSO. In these conditions, the voltammogram shows the redox couples Cu^{I}/Cu^0 (reduction ~ -0.72 V; oxidation ~ -0.45 V at $v = 0.1$ V/s) and Cu^{I}/Cu^{II} (oxidation at 0.53 V and reduction at 0.27 V for $v = 0.1$ V/s). The oxidation process seems to be monoelectronic versus ferrocene as standard in the same conditions. The system appears reversible even for low scan speed.

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*Experimental data: $c(L') = 10^{-3}$ mol/l; $E_{p\,ox} = 2.01$ V ($v = 0.1$ V/s); $I_p = 74$ μA ($v = 0.1$ V/s); $E_{1/2} = 2.12$ V ($\omega = 1000$ t/min); $I_D = 24.5$ μA ($\omega = 1000$ t/min).

Confirmation of the dimeric structure could be deduced from linear voltammetry which shows only one oxidative wave corresponding approximatively to a two-electron process while two waves, each being monoelectronic, are present during the reduction process.

Discussion

The redox properties of the metal centers are considerably modified by complexation with isocyanides. Since the redox potentials of the free cations are lower than those of the free ligands, complexation is needed to reach the potentials where the redox reactions occur.

When $CNCH_2SiMe_3$ (L) is used, the Mn^{II}/Mn^{I} and Mn^{I}/Mn^{0} values remain too low, making the reduction of Mn^{II} impossible. In considering the redox potential of Ag^{I}/Ag^{0}, formation of a silver mirror requires first complexation of Ag^+ and then electron transfer. The Cu complexes show a variety of redox reactions which are dependent on the stoichiometry of the complexes and the nature of the ligand and of the counter ion. The $Cu^{II}L_x/Cu^{I}L_x$ potentials are always lower than those of $L^{\circ+}/L$ as shown by cyclic voltammetry. Intermolecular reactions are eliminated since adding free ligand L increases slightly the current and does not yield the expected catalytic current on the $Cu^{I}L_x$ oxidation wave.

According to these results, the +1 oxidation state is the most stable for the copper complexes **1** and **2**. Oxidation into the Cu^{II} species yields oxidation of the ligand through an intramolecular process (reaction (1)).

$$Cu^{I}L_x \xrightarrow{-e^-} [Cu^{II}L_x]^* \longrightarrow [Cu^{I}L_{x-1}L^{\circ+}]^* \xrightarrow[+L]{} Cu^{I}L_x + [L^{\circ+}]^* \quad (1)$$

On the cathodic side, reduction of the complexes generates Cu^0 deposit on the electrode.

$CNCH_2SO_2C_7H_7$ behaves as expected for isocyanides [28, 29] and does not interfere with the redox reactions of the metal centers. Its reduction leads to the formation of Cu^0. Moreover, it acts as a bidentate bridging ligand in **4** being coordinated to the copper via the NC and SO_2 function as indicated by IR. Small shifts of $\nu_s(SO_2)$ and $\nu_{as}(SO_2)$ have also been observed in the two other compounds **5** and **8** indicating that this function can be perturbed even when the ligand is coordinated to copper or manganese centers only through the isocyanide function.

In conclusion, both isocyanides coordinate with copper and manganese salts giving rise to stable compounds, with different stereochemistries, ligand/metal ratio and oxidation states. The complexes are generally soluble in the usual organic solvents. Cu^{I} and mixed-valence Cu^{I}–Cu^{II} complexes were obtained. Mn^{II} compounds produce new mixed L_nMnX_2 complexes with ratio L/Mn = 4 (X = Cl) and 2 ($X = NO_3$). Homoleptic $[Mn(CNR)_6]^{2+}$ complexes which have been synthesized for CNR (R = Me, Ph, Et, Bu, $CH=CH_2$) were not observed here.

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