removed during the purification process. The analysis for iron confirms these assumptions. As pointed out in the following section, there is about 0.08 mol % iron present in a form which contributes measurably to ferromagnetism.

The estimated diamagnetic correction is a significant fraction of the uncorrected molar susceptibility, with the principal part coming from the THF groups. Errors in these corrections or unaccounted-for changes in these values with temperature would affect the final corrected values of the molar susceptibility of the YCS. The diamagnetic correction was subject to some uncertainty because of the way in which the value for THF was assigned. However, the uncertainty probably does not exceed approximately $\pm 50 \times 10^{-6}$ emu/mol out of a total of 416.4×10^{-6} emu/mol. Bau et al. showed that the room-temperature conformation of the THF rings, characterized as somewhat planar, transformed into the puckered arrangement by the time the temperature had been reduced to 80 K.[4] It is unlikely that this conformational shift would account for more than approximately $\pm 50 \times 10^{-6}$ emu/mol. Thus, the total uncertainty in the diamagnetic correction over the temperature range studied should not have exceeded approximately $\pm 100 \times 10^{-6}$ emu/mol, which is far less than both the magnitude and change with temperature of the susceptibility of YCS.

Slight temperature-dependent shifts in the structural symmetry about the iron site were considered. However, this possibility was ruled out on the basis of the results of the low-temperature neutron diffraction studies of YCS,[4] which did not give any evidence of the O_h symmetry distortion of the $[FeH]_6^{4-}$ units in going from room temperature to 80 K.

The fluctuation in the susceptibility below 180 K with an apparent maximum about 125 K is also difficult to explain. A susceptibility maximum is typical of antiferromagnetism, but none of the constituents or possible impurities are known as antiferromagnetic with Neél points in that temperature range.

Despite the presence of the residual paramagnetism the possibility of high-spin iron(II) can be ruled out on the basis of the magnitude of the observed susceptibility. If the iron were in the high-spin state, with the effective number of Bohr magnetons being approximately 5 μ_B, the susceptibility would be at least 10 times larger at 295 K and the variation with temperature would be characterized by a fourfold increase at 78 K.

The small ferromagnetic impurity noted above could possibly be contributed by colloidal sized particles of elemental iron and/or ferromagnetic iron oxide, Fe_3O_4. From the measured saturation magnetization of this component of approximately 10 emu/mol, the amount of elemental iron in this sample is estimated to be approximately 0.08 mol %.

The room-temperature Mössbauer spectrum of YCS showed a sharp single line with an isomer shift of +0.02 (1) mm/s. The reference material was metallic α-iron. The χ^2 value for the spectrum fit was 0.94 mm/s, and the line width, Γ, was 0.62 mm/s. No quadrupole splitting was observed, thus indicating the absence of any electric field gradient at the iron nucleus. This nonsplitting singlet is consistent with the O_h symmetry of the $[FeH]_6^{4-}$ units. Both the position of the isomer shift and absence of a quadrupole split are consistent with low-spin iron(II).

The other common oxidation states of iron, high-spin iron(II) and -(III) and low-spin iron(III), were not believed to be present on the basis of the following: (a) the value of the isomer shift, (b) the absence of the quadrupole splitting of the YCS complex, and (c) the well-known Mössbauer isomer shift and quadrupole splitting parameters[28] for these other oxidation states and crystal field orbital occupancies.

These Mössbauer results are entirely consistent with the conclusions drawn from the magnetic susceptibility data. Any impurities or other effects that might give rise to the observed residual paramagnetism may be at such a low concentration that they were not observed in the Mössbauer experiments.

Acknowledgment. We wish to acknowledge Allan Thomas, who collected some of the magnetic susceptibility data. S.S. and R.P.Z. acknowledge the support of the National Science Foundation under Grant NSF-CHE-8204417.

---

(28) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy", Chapman and Hall Ltd., London, 1971.

(29) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Contribution from the Departamentos de Química Inorgánica y Electroquímica,
Facultad de Ciencias, Universidad Autónoma de Madrid, 28049-Madrid, Spain

Syntheses and Variable-Temperature Mössbauer Study of Tin(IV) Cyanide Derivatives

D. TUDELA,*[1a] V. FERNÁNDEZ,[1a] and J. D. TORNERO[1b]

Received December 28, 1984

By reaction of $SnCl_4$ with Me_3SiCN in CCl_4 solution, the compound $SnCl_3CN(Me_3SiCN)$ was obtained. The oxidative-addition reactions of XCN (X = Br, I) to $SnCl_2$ in THF solutions lead to the formation of $SnCl_2XCN(THF)$ (X = Br, I). The three new compounds have bridging cyanide groups as inferred from their IR spectra. By means of a variable-temperature Mössbauer study, a polymeric structure has been proposed for $SnCl_3CN(Me_3SiCN)$ and $SnCl_2BrCN(THF)$, while an oligomeric structure would be possible for $SnCl_2ICN(THF)$. The Goldanskii–Karyagin effect is observed for $SnCl_3CN(Me_3SiCN)$ and might be present, as suggested by computer fitting, in $SnCl_2BrCN(THF)$. During the preparation of this last compound, a solid of approximate composition $SnCl_2BrCN(THF)_{1.5}$ was isolated; its Mössbauer spectra can be explained as a mixture of $SnCl_2BrCN(THF)$ and $SnCl_2BrCN(THF)_2$, suggesting a monomeric structure with the THF ligands in trans position for this last species.

Introduction

Organotin cyanides of the types R_3SnCN and $R_2Sn(CN)_2$ are well-known, but the corresponding inorganic derivatives have received little attention.[2] Organotin cyanides usually have polymeric structures,[3] and the Goldanskii–Karyagin effect has been detected in the Mössbauer spectra of Me_3SnCN.[4] Attempts to prepare $Sn(CN)_4$ from $SnCl_4$ and Me_3SiCN failed, and the formation of mixtures of compounds was observed.[5] Although Me_3SiCN is a useful tool for substitution reactions,[6] it can form

---

(1) (a) Departamento de Química Inorgánica. (b) Departamento de Electroquímica.

(2) Golub, A. M.; Köhler, H. "Chemie der Pseudohalogenide"; Dr. Alfred Hüthig Verlag: Heidelberg, FRG, 1979.

(3) Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251.

(4) Herber, R. H.; Chandra, S.; Hazony, Y. *J. Chem. Phys.* **1970**, *53*, 3330.

(5) Bither, T. A.; Knoth, W. H.; Lindsey, R. V., Jr.; Sharkey, W. H. *J. Am. Chem. Soc.* **1958**, *80*, 4151.

(6) Andersen, R. A. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 31.

0020-1669/85/1324-3892$01.50/0

Table I. ^{119}Sn Mössbauer Data for Tin(IV) Cyanide Derivatives

compd	IS,[a] mm s^{-1}	QS,[a] mm s^{-1}	Γ,[b] mm s^{-1}	d(ln A)/dT, $K^{-1} \times 10^{-2}$	r[c]	no. of points	temp range, K
$SnCl_3CN(Me_3SiCN)$	0.37	0.83	1.03	−1.00	0.997	8	$77 \leqslant T \leqslant 198$
$SnCl_2BrCN(THF)$	0.22	0.54	1.09	−1.32	0.997	7	$77 \leqslant T \leqslant 189$
$SnCl_2ICN(THF)$	0.56	1.27	1.27	−1.59	0.996	7	$77 \leqslant T \leqslant 187$
"$SnCl_2BrCN(THF)_{1.5}$"[d]				−1.56	0.9995	7	$77 \leqslant T \leqslant 192$
$SnCl_2BrCN(THF)$	0.22[e]	0.54[e]	1.00				
$SnCl_2BrCN(THF)_2$	0.58	1.28	1.03				

[a] At 77 K, ±0.02 mm s^{-1} except for $SnCl_2BrCN(THF)_2$, which obviously has larger errors. [b] Line widths uncorrected for sample thickness. [c] Correlation coefficient. [d] Spectra adjusted as a mixture of $SnCl_2BrCN(THF)$ and $SnCl_2BrCN(THF)_2$. [e] Fixed parameter.

addition compounds with some Lewis acids.[7] Following our interest in inorganic tin pseudohalides,[8,9] we have reinvestigated the reaction between $SnCl_4$ and Me_3SiCN and we have also tried to prepare tin cyanide derivatives by means of the oxidative-addition reactions of XCN (X = Br, I) to $SnCl_2$. A similar reaction between $SnCl_2$ and IN_3 has been previously reported.[10]

Experimental Section

Reactions were carried out under N_2 with dry solvents deoxygenated and purified by standard methods. Reagent grade $SnCl_2$ (BDH Chemical Ltd.) was used without further purification. Me_3SiCl, $SnBr_4$, and $SnCl_4$ were distilled before use. A solution of Me_3SiCN in CCl_4 was prepared according to a method described by Groutas and Felker,[11] and XCN compounds (X = Br, I) were prepared by using previously described methods.[12]

Infrared spectra were recorded as Nujol mulls on a Nicolet 5DX FT-IR spectrometer. Mössbauer spectra were obtained for the polycrystalline samples in transmission geometry by using a $Ca^{119}SnO_3$ source at room temperature. The constant-acceleration spectrometer, velocity calibration, sample holder and computation procedures have been described previously.[13] All isomer shifts are reported with respect to the center of a room-temperature $BaSnO_3$ reference spectrum. The maximum statistical error in the experimental points was 0.2%. The low-temperature cryostat used was a Ricor Ltd. Model MCH-5B in conjunction with a Ricor Ltd. Model TC-4B temperature controller. Temperature data were obtained with a suitably calibrated platinum resistance thermometer affixed directly to the cryogenic sample holder. Temperature stability during the accumulation of the spectra was better than ±0.5 K.

Preparations. $SnCl_3CN(Me_3SiCN)$. A 39-mmol sample of $SnCl_4$ was dropped with constant stirring into a solution of 39.8 mmol of Me_3SiCN in 40 mL of CCl_4 at room temperature. A white precipitate formed and gradually transformed into a gray solid, which was filtered off, washed with CCl_4, and vacuum-dried. The solid is insoluble in noncoordinating solvents and is very hygroscopic, fuming in moist air. Anal. Calcd (found): Sn, 33.88 (32.98); Cl, 30.36 (29.47); CN, 14.86 (13.06). Mp: decomposes around 90 °C.

$SnCl_2BrCN(THF)$. $SnCl_2$ (16.8 mmol) and BrCN (17.0 mmol) were allowed to react for 16 h in 25 mL of THF, with stirring, at room temperature. Afterward the solvent was eliminated by vacuum, leaving a white solid with a composition close to $SnCl_2BrCN(THF)_{1.5}$. Anal. Calcd (found): Sn, 29.64 (30.99); Cl, 17.71 (17.72); Br, 19.96 (19.29). This solid was maintained in vacuo (10^{-1} torr) at 40 °C for 4 days, and $SnCl_2BrCN(THF)$ could be isolated as a white hygroscopic solid, which decomposes upon contact with some organic solvents ($CHCl_3$, CH_2Cl_2, C_6H_6). Anal. Calcd (found): Sn, 32.28 (32.80); Cl, 19.29 (19.42); Br, 21.74 (21.38); CN, 7.08 (6.43). Mp: decomposes around 150 °C.

$SnCl_2ICN(THF)$. Following the procedure described above with $SnCl_2$ (12.4 mmol) and ICN (12.5 mmol), a yellow hygroscopic solid was obtained after vacuum elimination of the solvent. Anal. Calcd (found): Sn, 28.62 (28.17); Cl, 17.10 (16.57); I, 30.70 (29.92); CN, 6.28 (5.59). Mp: decomposes around 100 °C. Mol wt (by cryoscopic measurements in nitrobenzene): 1094 and 600 for concentrations of 1.57 and 0.89%, respectively (calculated mol wt for the monomer is 414.6).

Results and Discussion

Addition or substitution compounds could be formed by reaction of $SnCl_4$ with Me_3SiCN. In fact both processes take place as suggested by the formation of $SnCl_3CN(Me_3SiCN)$; an addition compound is probably formed in a first step followed by its decomposition to the final product:

$$SnCl_4 + 2Me_3SiCN \rightarrow SnCl_4(Me_3SiCN)_2 \rightarrow SnCl_3CN(Me_3SiCN) + Me_3SiCl$$

This reaction was attempted in 1958 by Bither et al.,[5] who were not able to isolate any definite compound, probably because the reaction was carried out in refluxing xylene (ca. 140 °C) while $SnCl_3CN(Me_3SiCN)$ decomposes around 90 °C. The IR spectrum of $SnCl_3CN(Me_3SiCN)$ indicates the presence of Me_3SiCN[14] and shows two strong bands at 2257 and 2201 cm^{-1}, which can be assigned to νCN. This band appears aroound 2190 cm^{-1} in the IR spectrum of free Me_3SiCN[14-16] and, like those of organic nitriles, must shift to higher frequencies when coordination to a metallic atom takes place.[17] Both νCN frequencies are in the range of bridging cyanide groups[18] and are consistent with a structure containing six-coordinate Sn(IV), via cyanide bridges, with coordinated Me_3SiCN groups.

Me_3SiCN is a very weak Lewis base and does not interact with $SnBr_4$ in such a way that the IR spectrum of a solution of Me_3SiCN and $SnBr_4$ in CCl_4 presents νCN at the same position as the that for free ligand.[14-16]

As a new way to prepare tin(IV) cyanide derivatives, we have studied the oxidative-addition reactions of cyanogen halides to tin(II) halides:

$$SnCl_2 + XCN \xrightarrow{THF} SnCl_2XCN(THF) \qquad X = Br, I$$

νCN appears at 2210 and 2209 cm^{-1} in the IR spectra of $SnCl_2BrCN(THF)$ and $SnCl_2ICN(THF)$, respectively, showing that both compounds have bridging CN groups.[18]

Variable-Temperature Mössbauer Study. The three tin(IV) cyanide derivatives previously described have the general formulas $SnCl_2XCNL$ (X = Cl, L = Me_3SiCN; X = Br, L = THF; X = I, L = THF) with CN bridging groups, so that they must be hexacoordinated, and their structure can be either of linear-chain polymers or of cyclic oligomers. Variable-temperature Mössbauer spectroscopy can help us to solve this problem, and the corresponding parameters are shown in Table I.

$SnCl_3CN(Me_3SiCN)$. While the quadrupole splitting (QS) of $SnCl_3CN(Me_3SiCN)$ (Table I) is essentially temperature independent in the range $77 \leqslant T \leqslant 291$ K, the isomer shift (IS) linearly decreases with temperature (dIS/dT = -3.04×10^{-4} mm s^{-1} K^{-1}, r = 0.992, 11 points) because of a second-order Doppler shift. The two components of the quadrupole doublet have practically the same line width (within ±0.03 mm s^{-1}) over the whole temperature range studied.

---

(7) Evers, E. C.; Freitag, W. O.; Keith, J. N.; Kriner, W. A.; MacDiarmid, A. G.; Sujishi, S. *J. Am. Chem. Soc.* **1959**, *81*, 4493.

(8) Fernåndez, V.; Tudela, D.; Masaguer, J. R. *An. Quim.* **1979**, *75*, 490.

(9) Tudela, D.; Fernåndez, V.; Tornero, J. D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 791.

(10) Dehnicke, K.; Ruschke, P. *Z. Anorg. Allg. Chem.* **1978**, *444*, 54.

(11) Groutas, W. C.; Felker, D. *Synthesis* **1980**, *11*, 861.

(12) Brauer, G. "Handbuch der Präparativen Anorganischen Chemie"; Ferdinand Enke Verlag: Stuttgart, FRG, 1978.

(13) Tudela, D.; Fernåndez, V.; Tornero, J. D. *Z. Anorg. Allg. Chem.* **1984**, *509*, 174.

(14) Booth, M. R.; Frankiss, S. G. *Spectrochim. Acta, Part A* **1970**, *26A*, 859.

(15) Seckar, J. A.; Thayer, J. S. *Inorg. Chem.* **1976**, *15*, 501.

(16) Szostak, R.; Hawranek, J. P. *Chem. Phys. Lett.* **1981**, *84*, 331.

(17) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley-Interscience: New York, 1970.

(18) Dows, D. A.; Haim, A.; Wilmarth, W. K. *J. Inorg. Nucl. Chem.* **1961**, *21*, 33.

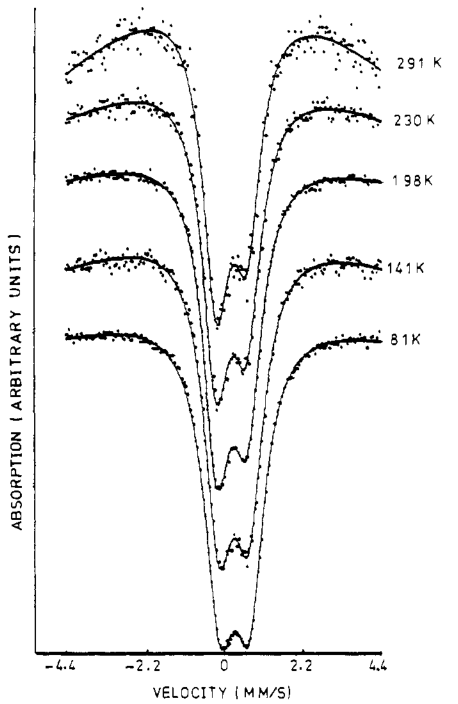

Figure 1. Mössbauer spectra of $SnCl_3CN(Me_3SiCN)$ at five temperatures.

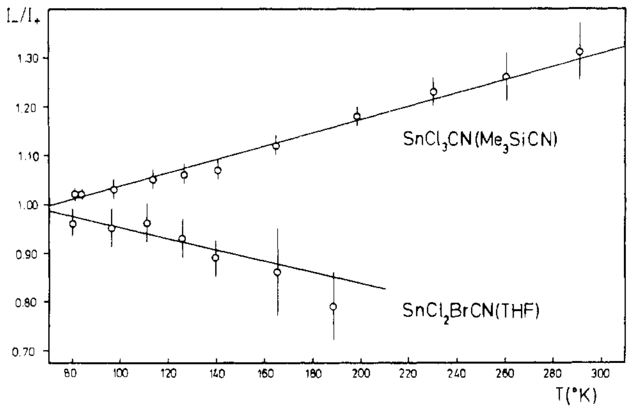

Figure 2. Plots of $I-/I+$ vs. temperature for $SnCl_3CN(Me_3SiCN)$ and $SnCl_2BrCN(THF)$. $I-$ and $I+$ are the areas under the resonance curve at more negative and more positive velocities than the spectrum centroid, respectively.

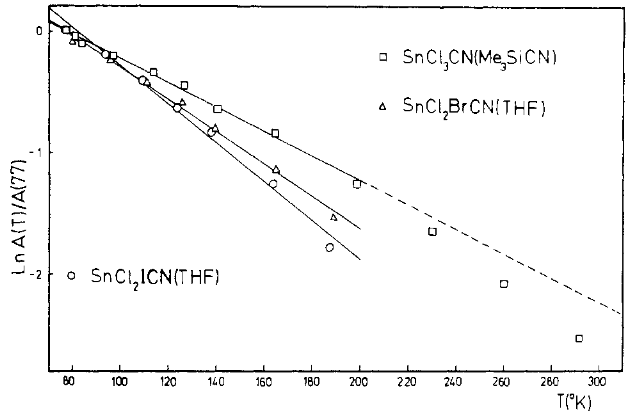

Figure 3. Plots of ln (A_T/A_{77}) vs. temperature for $SnCl_3CN(Me_3SiCN)$, $SnCl_2BrCN(THF)$, and $SnCl_2ICN(THF)$.

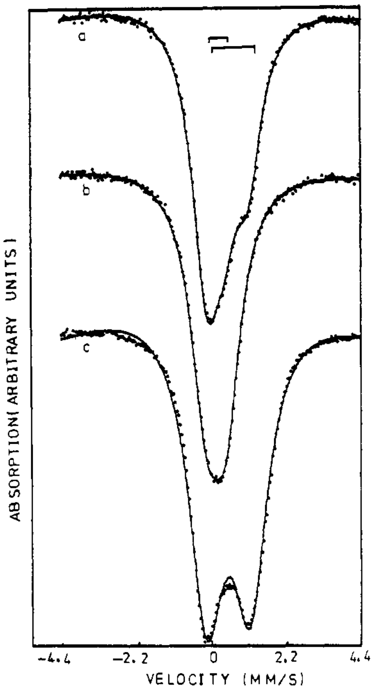

Figure 4. Mössbauer spectra at liquid-nitrogen temperature: (a) "$SnCl_2BrCN(THF)_{1.5}$", a mixture of $SnCl_2BrCN(THF)$ and $SnCl_2BrCN(THF)_2$; (b) $SnCl_2BrCN(THF)$; (c) $SnCl_2ICN(THF)$.

As shown in Figure 1, $SnCl_3CN(Me_3SiCN)$ gives a well-resolved Mössbauer spectrum (ca. 4% absorption) at room temperature; this fact strongly suggests a polymeric structure[19,20] but cannot be taken as conclusive evidence.[21] The Goldanskii–Karyagin effect arises from a lattice dynamic anisotropy in the recoil-free fraction and is manifested in a temperature-dependent doublet line asymmetry.[22] This phenomenon is present in $SnCl_3CN(Me_3SiCN)$ and is clearly visible in Figure 1, which shows that the asymmetry has virtually disappeared at liquid-N_2 temperature. The temperature dependence of the ratio $I-/I+$ is linear (slope = 1.4×10^{-3} K^{-1}, $r = 0.995$, 11 points) over the temperature range $77 \leq T \leq 291$ K, as shown in Figure 2. Such a linear behavior is not unprecedented.[23] Although the Goldanskii–Karyagin effect has been observed in some molecular solids,[24,25] it is often taken as suggestive of a polymeric structure.[19,20,23]

According to the Debye model the plot of ln A vs. temperature should be linear for thin absorbers in the high-temperature limit, and the slope of the straight line can give us information about the intermolecular association in the crystal lattice.[26] Plots of ln A (normalized to 77 K for ease of comparison) vs. temperature for the studied species are displayed in Figure 3; the data for $SnCl_3CN(Me_3SiCN)$ show a small but significant downward curvature over the entire range of temperatures studied (77–291 K) probably due to motional anharmonicity.[19] Nevertheless, a good regression line ($r = 0.997$) can be obtained in the range $77 \leq T \leq 198$ K, which suggests that anharmonicity effects are minima in this range. The slope d(ln A)/dT = -1.00×10^{-2} K^{-1}

---

(19) Molloy, K. C.; Bigwood, M. P.; Herber, R. H.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 3709.

(20) Cunningham, D.; Firtear, P.; Molloy, K. C.; Zuckerman, J. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1523.

(21) Bancroft, G. M.; Butler, K. D.; Sham, T. K. *J. Chem. Soc., Dalton Trans.* **1975**, 1483.

(22) Herber, R. H.; Chandra, S. *J. Chem. Phys.* **1971**, *54*, 1847.

(23) Ho, B. Y. K.; Molloy, K. C.; Zuckerman, J. J.; Reidinger, F.; Zubieta, J. A. *J. Organomet. Chem.* **1980**, *187*, 213.

(24) Herber, R. H.; Leahy, M. F.; Hazony, Y. *J. Chem. Phys.* **1974**, *60*, 5070.

(25) Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Curtui, M.; Guta, C.; Ruse, D. *Inorg. Chem.* **1980**, *19*, 2861.

(26) Harrison, P. G.; Phillips, R. C.; Thornton, E. W. *J. Chem. Soc., Chem. Commun.* **1977**, 603.

is clearly within the range associated with polymeric structures.[19,25–27]

$SnCl_2BrCN(THF)$. Figure 4 shows the Mössbauer spectrum of $SnCl_2BrCN(THF)$ at liquid-nitrogen temperature. The IS and QS values for this compound (Table I) are practically constant in the temperature range $77 \leqslant T \leqslant 189$ K. $SnCl_2BrCN(THF)$ gives a poor Mössbauer effect at room temperature (0.4% absorption), and although its spectra are unresolved quadrupole doublets, their computer fitting indicate a line asymmetry, which seems to be temperature-dependent (Figure 2) and might be due to the Goldanskii–Karyagin effect.

The plot of ln *A* vs. temperature for $SnCl_2BrCN(THF)$ (Figure 3) shows a small downward curvature over the entire range of temperatures studied (77–189 K); however, the experimental points can be fitted to a straight line ($r = 0.997$) with a slope -1.32×10^{-2} K^{-1}, which allows us to propose a polymeric structure for this compound,[19,20,28] similar to the one of $SnCl_3CN(Me_3SiCN)$.[29]

$SnCl_2ICN(THF)$. The Mössbauer spectrum of $SnCl_2ICN(THF)$ at liquid-nitrogen temperature (Figure 4) cannot be satisfactorily adjusted with only one quadupole doublet; this is even more evident, bearing in mind that $\chi^2 = 2105$,[30] and shows that more than one resonant species are present. We have fitted the seven registered spectra in the temperature range $77 \leqslant T \leqslant 187$ K with only a quadrupole doublet in order to study their evolution with temperature, because of the difficulties in fitting them with all the present species. The IS and QS values (Table I) display little changes with temperature, and the computed line asymmetry in the spectra is temperature insensitive ($I-/I+$ ranges between 1.07 and 1.09), showing no evidence of the Goldanskii–Karyagin effect. No ambient-temperature spectrum can be resolved for $SnCl_2ICN(THF)$. Although the plot of ln *A*. vs. temperature also shows some downward curvature (Figure 3), a regression straight line ($r = 0.996$) can be obtained with a slope, $d(\ln A)/dT = -1.59 \times 10^{-2}$ K^{-1}. Similar temperature coefficients have been found for solids comprising noninteracting molecules,[19,28,31] so that an oligomeric structure would be possible for $SnCl_2ICN(THF)$. On the other hand, cryoscopic measurements in nitrobenzene indicate a greater association degree than the one corresponding to a dimer.

"$SnCl_2BrCN(THF)_{1.5}$". By reaction of $SnCl_2$ with BrCN in THF solution we initially isolated a solid of approximate composition $SnCl_2BrCN(THF)_{1.5}$, whose Mössbauer spectrum (Figure 4) indicates the presence of more than one species and can be explained as a mixture of $SnCl_2BrCN(THF)$ and $SnCl_2BrCN(THF)_2$. According to this interpretation, the initial product of the reaction is $SnCl_2BrCN(THF)_2$, which afterward loses a molecule of THF, giving rise to $SnCl_2BrCN(THF)$. In fact, when "$SnCl_2BrCN(THF)_{1.5}$" is kept in vacuo, at a moderate temperature, the final product is exclusively $SnCl_2BrCN(THF)$. Both "$SnCl_2BrCN(THF)_{1.5}$" and $SnCl_2BrCN(THF)$ have practically the same IR spectra. The lack of νCN corresponding to $SnCl_2BrCN(THF)_2$ could be due to the fact that, although CN terminal groups display νCN at lower frequencies than the bridging ones,[18] its intensity is generally weaker[32] and could be masked by the band at 2210 cm^{-1} of $SnCl_2BrCN(THF)$. The Mössbauer spectra of "$SnCl_2BrCN(THF)_{1.5}$" were fitted with two quadrupole doublets; for the one corresponding to $SnCl_2BrCN(THF)$, the IS, QS, and intensity ratio were constrained to the previously found values. In this way, the parameters shown in Table I were obtained. Due to the overlapping nature of the spectra the intensities corresponding to each species are subject to considerable error, thus precluding the determination of the temperature dependence of ln *A* for $SnCl_2BrCN(THF)_2$. However, Table I shows the temperature dependence of the total area under the spectra, and considering the value previously found for $SnCl_2BrCN(THF)$ (1.32×10^{-2} K^{-1}), the temperature coefficient for $SnCl_2BrCN(THF)_2$ must be higher than 1.56×10^{-2} K^{-1}. That agrees[19,28,31] with the monomeric structure that was expected because the tin atom is hexacoordinated without the need of using cyanide bridges. The IS and QS for $SnCl_2BrCN(THF)_2$ resemble those measured for $SnCl_2Br_2(THF)_2$,[13] corresponding to the similarity between both compounds, which implies that the THF groups coordinate in the trans position.

Registry No. $SnCl_3CN(Me_3SiCN)$, 98586-97-1; $SnCl_2BrCN(THF)$, 98586-98-2; $SnCl_2ICN(THF)$, 98586-99-3; $SnCl_2BrCN(THF)_2$, 98587-00-9; $SnCl_2$, 7772-99-8; BrCN, 506-68-3; ICN, 506-78-5.

---

(27) Harrison, P. G.; Sharpe, N. W.; Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Chem. Soc., Dalton Trans.* **1983**, 921.

(28) Harrison, P. G.; Lambert, K.; King, T. J.; Majee, B. *J. Chem. Soc., Dalton Trans.* **1983**, 363.

(29) An approximate point charge model calculation suggests that $SnCl_3CN(Me_3SiCN)$ and $SnCl_2BrCN(THF)$ might have a different sign of the quadrupole splitting. This fact could explain the different behavior in line asymmetry, which can be seen in Figure 2.

(30) With 192 degrees of freedom; for the other compounds χ^2 ranges between 237 and 330 under the same conditions.

(31) Harrison, P. G.; Sharpe, N. W.; Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Chem. Soc., Dalton Trans* **1983**, 1687.

(32) Casabó, J.; Ribas, J. *J. Inorg. Nucl. Chem.* **1977**, *39*, 147.

Contribution from the Department of Chemistry,
Brookhaven National Laboratory, Upton, New York 11973

Pulse-Radiolysis Study of Mixed-Valence $Mo^{IV,V}$ Complexes of EDTA, L-Cysteine, and Oxalate

JAMES D. RUSH and BENON H. J. BIELSKI*

Received June 11, 1985

The molybdenum(IV,V) mixed-valence complexes $Mo^{IV}Mo^{V}O_4L_n^{2-}$, where L_n = (EDTA), (L-cyst)$_2$, or $(ox)_2(H_2O)_2$, were obtained by pulse-radiolytic reduction of the corresponding Mo^V complexes with the hydrated electron, e_{aq}^-. The rates of reduction for the various complexes were found to be similar; $k_4 = k_5 = (1.5 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}. The mixed-valence complexes can also be generated by reduction of the parent complexes with Zn^+ ($k_6 \sim k_7 \simeq 5 \times 10^9$ M^{-1} s^{-1}). The Mo(IV,V) mixed-valence complexes absorb weakly in the visible range ($\epsilon \sim$ 300–500 M^{-1} cm^{-1}). While in the absence of oxygen their decay is relatively slow ($t_{1/2} \sim$ 5–10 s) and does not result in Mo(III) product formation, in the presence of O_2 they undergo rapid second-order oxidation ($k \sim 10^8$ M^{-1} s^{-1}) back to the Mo(V) complexes. The latter observation suggests that the driving force for regeneration of the $Mo^V{}_2O_4^{2+}$ unit is sufficient to cause reduction of the ligands in the reduced complex. Substitution of the bridging oxides in the EDTA complex with sulfide does not significantly change the stability of the mixed-valence complex.

Introduction

The aqueous chemistry of molybdenum in its higher oxidation states (IV, V, VI) is characterized by the formation of polymeric species, and the structures of numerous complexes of molybdenum(V) and -(VI) have been determined.[1,2] Interest in these complexes has been partly due to the importance of molybdenum

---

(1) Ardon, M.; Pernick, A. *J. Less-Common Met.* **1977**, *54*, 233.

0020-1669/85/1324-3895$01.50/0