Correlation of Fe^{II} Low-spin Mössbauer Quadrupole Splittings and the $^1T_1$ Splitting in the Electronic Spectra of Iron(II) Isocyanide Compounds. The Oxidation State of Tin in the Tin Trichloride Ligand

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The electronic spectra of five iron(II)–isocyanide complexes of general formula *trans*- and *cis*-$FeX_2(ArNC)_4$ (X = Cl and/or $SnCl_3$; ArNC = *p*-methoxyphenyl isocyanide) and the cationic complex $[Fe(SnCl_3)(ArNC)_5]^+ClO_4^-$ have been recorded and assigned. Splitting of the excited $^1T_{1g}$ state has been observed for the first time in Fe^{II} low-spin compounds. As predicted previously, the splitting of the $^1T_1$ state (Δ^1T_1) correlates with the ^{57}Fe quadrupole splitting. In the compounds containing the $SnCl_3$ ligand, the Sn has a formal oxidation state of Sn^{II}, yet the ^{119}Sn Mössbauer centre shift (c.s.) lies in the ' Sn^{IV} region '. The value of the Sn Mössbauer c.s. for assigning the oxidation state and valency of Sn in Sn–metal compounds is discussed.

THE electronic spectra of Co^{III} compounds are well characterized, and they have been of fundamental importance in establishing the spectrochemical ranking of ligands (for example, see references 1—5, and references therein). In contrast, very few electronic spectra of the isoelectronic Fe^{II} low-spin species have been reported,[4,6] and the splitting of the excited $^1T_1$ (Δ^1T_1) and/or $^1T_2$ states has not been visually resolved, although the spectrum of $Na_2Fe(CN)_5NO,2H_2O$ [6] shows very weak shoulders above 30,000 cm^{-1} which have been assigned to the components of the $^1A_1 \rightarrow {}^1T_1$, and $^1A_1 \rightarrow {}^1T_2$ transitions. Using arguments presented previously,[5,7,8] there should be a correlation between the ^{57}Fe quadrupole splitting (q.s.) and Δ^1T_1 for Fe^{II} low-spin compounds. Choosing compounds with comparatively large q.s. values, we have resolved the splitting of the $^1T_1$ state for two compounds, and report a correlation between q.s. and Δ^1T_1.

The formal oxidation state of Sn in such compounds as *trans*- and *cis*-$Fe(ArNC)_4(SnCl_3)_2$ is Sn^{II}, given that the oxidation state of Fe is Fe^{II}. ^{119}Sn Mössbauer spectra show that the c.s. values lie in what is normally considered to be the Sn^{IV} region. These results indicate strongly that the Mössbauer centre shift cannot be used as suggested by Fenton and Zuckerman,[9] to assign formal oxidation states of Sn. Rather, the results support the suggestion of Lappert *et al.*[10] that the Sn Mössbauer c.s. should more properly be used to assign the valency of Sn.

EXPERIMENTAL

All compounds were prepared as reported previously.[11] Electronic spectra were taken using a Beckman DK/1 spectrophotometer for chloroform solutions, and a standard Cary 14 instrument with a specially constructed reflectance attachment for solid-state spectra.

Sn Mössbauer spectra were recorded at 80 K using a $BaSnO_3$ source and an Austin Science Associates spectrometer. Calibrations were taken both with a laser interferometer and natural iron foil at room temperature. All c.s. values are quoted with respect to the $BaSnO_3$ source, using the scan centre of the mirror image spectra as a zero velocity standard.

RESULTS AND DISCUSSION

Electronic Spectra and Correlation with Quadrupole Splittings.—The reflectance spectra of *trans*-$FeCl_2(ArNC)_4$, *trans*-$Fe(SnCl_3)_2(ArNC)_4$, and *cis*-$FeCl_2(ArNC)_4$ are shown in Figure 1, and the positions of the peaks are given in Table 1 along with the proposed assignments and the ^{57}Fe quadrupole splittings previously obtained.[7] We use the reflectance spectra for further discussion for three reasons. Firstly, no spectrum of *cis*-$FeCl_2(ArNC)_4$ could be obtained in solution since it isomerizes rapidly to the *trans*-form.[11] Secondly, slightly better resolution was obtained for the reflectance spectra (with the exception of $[Fe(ArNC)_5SnCl_3]ClO_4$). Thirdly, Mössbauer spectra are obtained in the solid state, and it is thus desirable to correlate results for both types of spectra in the solid.

The spectra (Figure 1 and Table 1) are qualitatively similar to Co^{III} spectra,[1,2] but the charge-transfer band at about 30,000 cm^{-1} has made it difficult to resolve more than one peak in the Fe^{II} spectra.[7] However, for the two *trans*-compounds, *trans*-$FeCl_2(ArNC)_4$ and *trans*-$Fe(SnCl_3)_2(ArNC)_4$, two bands of comparable intensity are clearly resolved (Figure 1).

In an octahedral d^6 low-spin compound, two spin-allowed transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are often resolved; in C_{4v} or D_{4h} symmetry, both of these bands split into two.[3-5] The two resolved peaks in the two *trans*-compounds (D_{4h} symmetry) could be assigned in two ways: the two peaks to unresolved $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, or to the resolved components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition, *i.e.* $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$. Since the separation of $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ bands in Co^{III} compounds is always greater than 5,000 cm^{-1},[3-5] we assign the two resolved bands in the *trans*-compounds to the resolved components

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[1] M. Linhard and M. Weigh, *Z. anorg. Chem.*, 1952, **271**, 101.
[2] M. Linhard and M. Weigh, *Z. anorg. Chem.*, 1951, **264**, 321.
[3] C. J. Ballhausen, ' An Introduction to Ligand Field Theory,' McGraw-Hill, 1962, New York, ch. 5 and 10.
[4] A. B. P. Lever, ' Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968, ch. 7 and 9.
[5] D. S. McLure, *Adv. Chem. Co-ord. Compd.*, 1961, 498.
[6] P. T. Manohoran and H. B. Gray, *J. Amer. Chem. Soc.*, 1965, **87**, 3340.
[7] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc.* (*A*), 1970, 956.
[8] M. G. Clark, *Mol. Phys.*, 1971, **20**, 257.
[9] E. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, 1969, **8**, 1771.
[10] S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 1311.
[11] M. J. Mays and B. E. Prater, *J. Chem. Soc.* (*A*), 1969, 2525.

of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition, *i.e.* ${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$. Δ^1T_{1g} For *trans*-$FeCl_2(ArNC)_4$ and *trans*-$Fe(SnCl_3)_2(ArNC)_4$ are thus 3200 and 2100 cm^{-1} respectively.

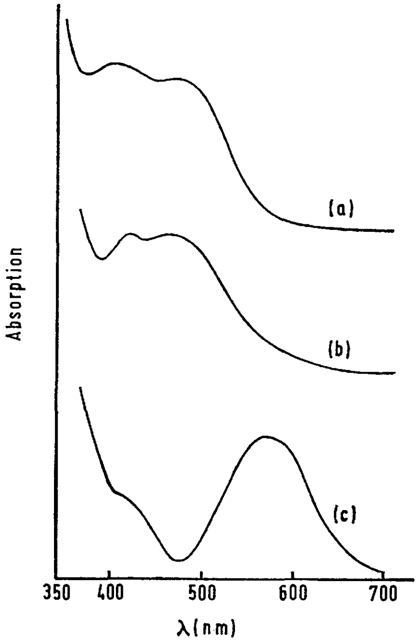

FIGURE 1 Reflectance spectra of (a) *trans*-$FeCl_2(ArNC)_4$, (b) *trans*-$Fe(SnCl_3)_2(ArNC)_4$, and (c) *cis*-$FeCl_2(ArNC)_4$

Other evidence strongly supports the above assignment. In *cis*-$FeCl_2(ArNC)_4$, one broad peak is resolved, and one shoulder is apparent on the edge of the charge-transfer band. This spectrum is very similar to *cis*-Co^{III} spectra,[1,2] and it can be assigned as for these *cis*-Co^{III} compounds: the low-energy band to the unresolved ${}^1A_1 \rightarrow {}^1T_1$ transition, and the high-energy shoulder to the ${}^1A_1 \rightarrow {}^1T_2$ transition. From the resolution of the peaks in the *trans*-compounds, the splitting of the ${}^1T_1$ level must be less than 1600 cm^{-1} in *cis*-$FeCl_2(ArNC)_4$. Since a 2 : 1 *trans* : *cis* ratio of Δ^1T_1 is expected, the *trans*- and *cis*-observed values of 3200 cm^{-1} and less than 1600 cm^{-1} respectively support the assignment of bands in both compounds.

TABLE 1

Fe^{II} Electronic spectra

Compound[b]	Peak positions (cm^{-1}) Reflectance	Absorption (CHCl$_3$ solution)	Assignment	Δ^1T_1 (cm^{-1}) (from reflectance spectrum)	^{57}Fe q.s.[a] (mm s^{-1})
trans-$FeCl_2(ArNC)_4$	21,000 24,200	20,400—21,500sh 24,800	${}^1A_{1g} \rightarrow {}^1E_g$ ${}^1A_{1g} \rightarrow {}^1A_{2g}$	3200	1·55
trans-$Fe(SnCl_3)_2(ArNC)_4$	21,700 23,800	24,300	${}^1A_{1g} \rightarrow {}^1E_g$ ${}^1A_{1g} \rightarrow {}^1A_{2g}$	2100	1·05
cis-$FeCl_2(ArNC)_4$	17,400 21,700—24,100sh	*c*	${}^1A_1 \rightarrow {}^1T_1$ ${}^1A_1 \rightarrow {}^1T_2$	<1600	0·78
cis-$FeCl(SnCl_3)(ArNC)_4$	18,900—20,800sh 23,600	19,800—21,700sh 24,300	${}^1A_1 \rightarrow {}^1T_1$ ${}^1A_1 \rightarrow {}^1T_2$	<1600	0·61
cis-$Fe(SnCl_3)_2(ArNC)_4$	18,000—20,600sh	23,800—26,700sh	${}^1A_1 \rightarrow {}^1T_1$	<1600	0·50
$[Fe(ArNC)_5SnCl_3]ClO_4$	Not resolved	24,400—27,000sh	${}^1A_1 \rightarrow {}^1T_1$	<1600	0·32

[a] Room-temperature values given in ref. 7. [b] ArNC = *p*-methoxyphenyl isocyanide. [c] Not stable in solution, isomerizes to *trans*-isomer (ref. 11).

In addition, as predicted earlier,[7,8] there is a positive correlation between the ^{57}Fe q.s. values[7] and Δ^1T_1 for the first three compounds in Table 1. Indeed, the ratios of $|\Delta^1T_1 : \text{q.s.}|$ for *trans*-$FeCl_2(ArNC)_4$ (2100) and *trans*-$Fe(SnCl_3)_2(ArNC)_4$ (2000) agree within the experimental error. This correlation again strongly supports the assignment of peaks in these three compounds.

The assignment of the two bands in *cis*-$FeCl(SnCl_3)(ArNC)_4$ cannot be made unambiguously. Because of the small q.s. for this compound (and the small expected Δ^1T_1), we tentatively assign the two peaks to the unresolved ${}^1A_1 \rightarrow {}^1T_1$ and ${}^1A_1 \rightarrow {}^1T_2$ transitions. The other two spectra of *cis*-$Fe(SnCl_3)_2(ArNC)_4$ and $[Fe(ArNC)_5SnCl_3]ClO_4$ gave poorly resolved shoulders on the edge of the charge transfer bands and these shoulders are assigned to the ${}^1A_1 \rightarrow {}^1T_1$ transition.

The Oxidation State and Valency of Tin.—The above electronic spectra, and the previously analysed Mössbauer spectra[7] show conclusively that iron in these compounds is in the Fe^{II} low-spin state. The Sn must then be present formally as Sn^{II}. For example, in the ^{57}Fe Mössbauer spectra,[7] both the c.s. and q.s. are additive for these compounds. If the Sn was present as Sn^{IV} in these compounds, the oxidation state of iron would change from Fe^{II} in $FeCl_2(ArNC)_4$ to Fe^0 in *cis*-$FeCl(SnCl_3)(ArNC)_4$ to Fe^{-II} in $Fe(SnCl_3)_2(ArNC)_4$, and the c.s. and q.s. would not be additive.

However, the ^{119}Sn Mössbauer parameters for these compounds (Table 2) are surprising for Sn^{II} compounds.* All spectra are very similar, and give c.s. values which are much lower than those for previously reported Sn^{II} compounds. For example, Sn^{II} compounds invariably give centre shifts above 2·65 mm s^{-1}, and Sn^{IV} compounds give centre shifts below this value.[9] Our c.s. values for Sn^{II} compounds thus lie in the ' Sn^{IV} region ' and constitute the first well defined exception to the use of 2·65 mm s^{-1} as the Sn^{IV}–Sn^{II} borderline. Clearly, c.s.

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* Sn^{II} and Sn^{IV} refer of course to *oxidation state* 2 and 4 respectively.

values for such Sn compounds cannot be used to define the *oxidation state* of Sn as suggested by Fenton and Zuckerman.[9]

It is probably more reasonable, as Lappert *et al.*[10] have suggested, to use the c.s. as a measure of the valency of the tin: in all M–$SnCl_3$ (M = metal) compounds, the *valency* of the tin is four.

TABLE 2

^{119}Sn Mössbauer parameters (mm s^{-1} at 80 K) [a]

Compound	c.s.[b]	q.s.
trans-$Fe(SnCl_3)_2(ArNC)_4$	1·88 ± 0·02	1·72 ± 0·02
cis-$Fe(SnCl_3)_2(ArNC)_4$	1·82 ± 0·02	1·74 ± 0·02
cis-$FeCl(SnCl_3)(ArNC)_4$	2·02 ± 0·05	1·77 ± 0·05
$[Fe(ArNC)_5SnCl_3]ClO_4$	1·85 ± 0·10	1·70 ± 0·10

[a] All full widths at half maximum are 1·05 ± 0·10 mm s^{-1}. [b] With respect to $BaSnO_3$ source.

The very low c.s. for these Sn^{II} compounds does not appear to be unreasonable. The lone pair in the $Sn^{II}Cl_3^-$ entity has a high *s* character,[10,12,13] and donation of this lone pair on bonding to Fe or other metals will thus decrease $[\psi(0)s]^2$ (and therefore the c.s.) considerably from those observed in the $SnCl_3^-$ ion (3·54 mm s^{-1}).[9] Any π back-donation to the Sn will also decrease the c.s.

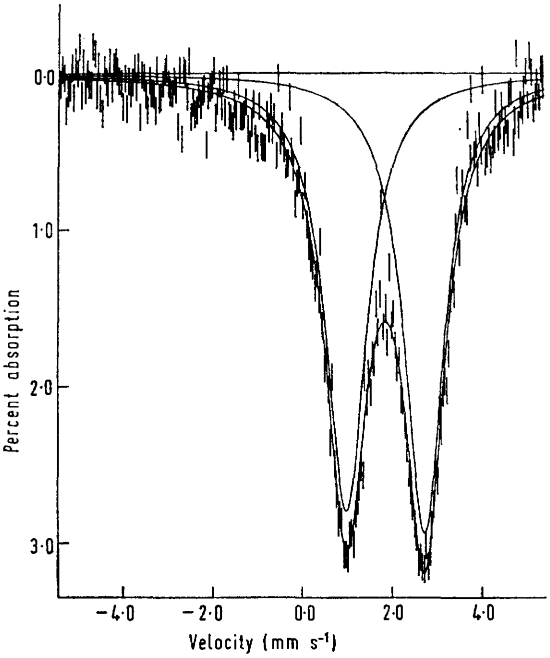

FIGURE 2 Mössbauer spectrum of *cis*-$Fe(SnCl_3)_2(ArNC)_4$ at 80 K

The resulting c.s. for all M–$SnCl_3$ compounds lie in the range 1·5—2·0 mm s^{-1} (ref. 10, 12—15) (in the Sn^{IV} region) whether or not the Sn is considered to have a formal oxidation state of two or four. Therefore Sn atoms in these compounds end up with very similar electronic environments whether or not the $SnCl_3$ complex was prepared from a Sn^{II} compound or a Sn^{IV} compound. Indeed, the same compound, such as $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$, can be prepared from Sn^{II} or Sn^{IV} precursors.[16,17] Our results show that the formal oxidation state of Sn in $SnCl_3$ complexes has significance *only* when the oxidation state of the other atoms and ligands is well defined. However, the valency of Sn in all $SnCl_3$ complexes is four.

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[12] D. E. Fenton and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, **90**, 6226.

[13] R. V. Parish, *Progr. Inorg. Chem.*, 1972, in the press.

[14] G. W. Parshall, *J. Amer. Chem. Soc.*, 1966, **88**, 704.

[15] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, in the press.

[16] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179.

[17] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.