Inorganica Chimica Acta, 76 (1983) L7–L8

Coordination Chemistry of Organometallic Bases of Group IV Elements:
Part VI*. Adducts of μ-oxo-bis[tri-n-butyltin(IV)] with Cobalt(II) and Iron(III) Chlorides

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Received August 6, 1982

In our earlier communications we have reported the coordination compounds obtained from the reactions of oxo-bis[triorganotin(IV)] and di-n-butyltin oxide with some common Lewis acids [1, 2] and liquid sulphur trioxide [3]. A few complexes have also been isolated with nickel(II) chloride in absolute alcohol [4]. We now report the synthesis and structural investigations of adducts of μ-oxo-bis[tri-n-butyltin(IV)] with cobalt(II) and iron(III) chlorides.

Experimental

μ-Oxo-bis[tri-n-butyltin(IV)] (Akzo Chemicals, Kirby, U.K.) was used as obtained. Cobalt(II) and iron(III) chlorides were dehydrated with thionyl chloride [12].

Preparation of Adducts

To a solution of μ-oxo-bis[tri-n-butyltin(IV)] in dry carbon tetrachloride was added dropwise a solution of cobalt(II) chloride in acetonitrile or iron(III) chloride in tetrahydrofuran in different molar ratios, at ice-bath (0–5 °C) temperature and in an atmosphere of dry nitrogen. After the addition, reddish brown solids were separated out. The contents of the flask were kept overnight for the completion of the reaction. The complexes were then filtered in an atmosphere of dry nitrogen, washed with dry carbon tetrachloride, dried *in vacuo* (1–2 mm) and analysed. The physical and analytical data of the complexes are given in Table I.

Physical Measurements

Infrared spectra of the complexes were recorded in KBr or fluorolube on a Perkin-Elmer Model 621 spectrophotometer. Reflectance spectra were taken on a SP 700 spectrophotometer using magnesium carbonate as the reference. Magnetic susceptibility measurements were carried out at room temperature on Gouy's balance.

Results and Discussion

The adducts are reddish-brown solids which decompose on heating. All these compounds are insoluble in common organic solvents.

The infrared spectrum of μ-oxo-bis[tri-n-butyltin(IV)] shows a sharp band at 784 cm^{-1} due to ν_{as}Sn–O–Sn modes [5]. On adduct formation (Table II) this shifts to a lower frequency region, by 54–69 cm^{-1}. New broad bands are also observed in the regions 420–400 and 460–410 cm^{-1} in the adducts of cobalt(II) and iron(III) chlorides respectively. These are assigned to O → M vibrations [6–8]. These observations indicate that the oxygen atom is the donor site in the ligand [1–3]. The appearance of sharp bands at 2171 and 2164 cm^{-1} due to νC≡N modes in the cobalt(II) complexes

TABLE I. Physical and Analytical Data of the Complexes.

Complex	Colour and State	Analysis Found (Calc.) %[a]		
		Co/Fe	Sn	Cl
$CoL \cdot Cl_2 \cdot CH_3CN$	Reddish–brown Powder	7.24 (7.68)	30.62 (30.92)	10.00 (9.26)
$CoL \cdot Cl_4 \cdot 3CH_3CN$	Reddish–brown Powder	11.98 (12.04)	23.92 (24.26)	15.02 (14.51)
$FeL \cdot Cl_3 \cdot THF$	Reddish–brown crystalline	6.58 (6.72)	28.50 (28.61)	13.60 (12.83)
$Fe_2LCl_6 \cdot 3THF$	Reddish–brown Powder	9.78 (9.82)	20.49 (20.89)	18.90 (18.75)

[a] Metal, tin and chlorine were estimated by the standard methods [12].

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*Part V, Polyhedron, 1982 (in press).

00020-1693/83/0000-0000/$03.00

TABLE II. Infrared Spectral Data of the Complexes (cm^{-1}).

$Co(L{\cdot}S^*)Cl_2$[a]	$Co_2(L{\cdot}3S^*)Cl_4$[a]	$Fe(L{\cdot}S^{**})Cl_3$[a]	$Fe_2(L{\cdot}S^{**})Cl_6$[a]	Assignments
2171m	2164m			$\nu C{\equiv}N$
		1040m	1053m	$\nu C{-}O{-}C$
730s	715s,br	718s	716s	ν_{as} Sn–O–Sn
668s	665s,br	667s		$\rho CH_3{\cdot}CH_2$
578m			572s	ν_{as} Sn–C_3
	509m	511m		ν_s Sn–C_3
415s	400m	410m,br 416s,br	422–446s,br	$\nu O \rightarrow M$

[a]S* = CH_3CN and S** = THF.

suggest that some coordinating sites are still occupied by the acetonitrile molecules. Similarly, the presence of νC–O–C modes at 1053 and 1040 cm^{-1} in the spectra of iron(III) complexes indicate the similar situation for iron(III) chloride and tetrahydrofuran. νM–Cl absorptions occur below 200 cm^{-1} in the case of octahedral complexes [9]. The spectra of the cobalt(II) and iron(III) complexes do not show any νM–Cl mode upto 250 cm^{-1}, which indirectly suggests the octahedral geometry of the complexes.

Reflectance spectra of the cobalt(II) complexes show two bands, with maximum absorptions in the regions 18.00–16.67 and 11.55–11.36 kK: typical of octahedral cobalt(II) complexes [10]. The former bands are assigned to ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transitions while the latter ones may be due to ligand transitions. Two bands are observed in the regions 9.88–9.63 and 14.88–14.70 kK in the reflectance spectra of iron(III) complexes, attributed to ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(S)$ and ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(S)$ transitions respectively. These transitions are in accordance with the six-coordinated iron(III) complexes [11].

Thus, on the basis of infrared and electronic spectra, colour, solubility in both polar and non-polar solvents and high melting points, we propose polymeric octahedral structures for these complexes.

The magnetic moment values at room temperature of cobalt(II) complexes have been found to lie in the range of 6.97–6.81 B.M. The magnetic moment of 1:1 iron(III) complex is found to be 7.12 B.M. These values are higher than the expected values (even those predicted from the full orbital contribution) for octahedral complexes of these metal chlorides. Thus, it may be inferred that either these adducts are ferromagnetic or magnetically concentrated substances, as reported earlier in case of nickel(II) complexes [4].

Acknowledgements

R.K.S. and H.K.S. are grateful to CSIR, New Delhi, for senior and postdoctoral research fellowships.

References

1 R. C. Paul, V. K. Mahajan, S. C. Ahluwalia, R. K. Sharma and S. P. Narula, *Inorg. Nucl. Chem. Lett., 9,* 893 (1973).

2 S. P. Narula and R. K. Sharma, *Indian J. Chem., 17A,* 98 (1979).

3 R. C. Paul, R. K. Sharma, R. Walia and S. P. Narula, *Indian J. Chem., 16A,* 544 (1978).

4 S. P. Narula and R. K. Sharma, *Indian J. Chem., 19A,* 769 (1980).

5 H. Kriegsmann, H. Hoffmann and H. Geissler, *Z. anorg. allg. Chem., 341,* 24 (1965).

6 A. N. Speca, L. L. Pytlewski and N. M. Karayannis, *J. Inorg. Nucl. Chem., 36,* 1227 (1974).

7 A. N. Speca, N. M. Karayannis and L. L. Pytlewski, *Inorg. Chim. Acta, 9,* 87 (1974).

8 A. N. Speca, N. M. Karayannis, L. L. Pytlewski, L. J. Winters and D. Kandasamy, *Inorg. Chem., 12,* 1221 (1973).

9 R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4,* 350 (1965).

10 D. P. Graddon, K. B. Heng and E. C. Watton, *Aust. J. Chem., 21,* 121 (1968).

11 E. Kokot, G. M. Mockler and G. L. Sefton, *Aust. J. Chem., 26,* 2105 (1973).

12 A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis', Longmans, London (1961).