Inorganica Chimica Acta, 16 (1976) L13 - L14

2-Hydroxycyclohepta-2,4,6-trienonato (Tropolonato) Derivatives of Bivalent Tin and Lead

A. RODGERS and S. R. STOBART

Department of Chemistry, Queen's University, Belfast BT9 5AG, N. Ireland

Received October 27, 1975

The chelating behaviour of 2-hydroxycyclohepta-2,4,6-trienone (tropolone) and related derivatives towards metals has been extensively investigated by Muetterties and co-workers, mainly with a view to establishing high coordination numbers at transition metal centres.[1] Renewed interest in the chemistry of bivalent compounds of the group 4B elements[2-4] has led us to explore the properties of some such species with tropolone as a ligand.

Results and Discussion

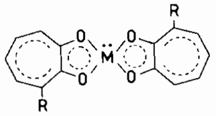
On slow addition of triethylamine to tin(II) chloride and tropolone (1:2 mol ratio) in anhydrous THF, the solution turned yellow and after filtration and recrystallization bis(tropolonato)tin(II) (I) was isolated (70%). A similar reaction with β-thujaplicin (2-hydroxy-4-isopropylcyclohepta-2,4,6-trienone) afforded the analogous thujaplicinato compound (II); the related lead(II) derivatives (III) and (IV) were synthesized in the same way using $PbCl_2$:

$$MCl_2 + 2(Chel)H \xrightarrow{NEt_3} M(Chel)_2$$

(M = Sn or Pb, Chel = tropolonato or β-thujaplicinato)

Physical and analytical data are collected in Table I. Compounds (I) and (II) were also produced in high yield from reactions of the tropolones with bis(cyclopentadienyl)tin(II)[6] in benzene, while reactions between lead powder and the appropriate tropolone derivative in boiling toluene provided an alternative route to compounds (III) or (IV).

Coordination of the tropolones to tin or lead was accompanied by lowering in energy of bands due to ν(C=O) in the i.r. (Table I) and by disappearance from the ^1H n.m.r. spectra of resonances near τ 0.7 due to the 1-hydroxy protons. These results imply bidentate attachment to the metal atom, and molecular weight measurements (Table I) as well as mass spectral data establish that compounds (I) - (IV) are monomeric and can be represented by the formulation (V).



(V; M = Sn or Pb, R = H or iso-C_3H_7)

Support for the bivalent character of the metal in the tin compounds (I) and (II) is provided by ^{119m}Sn Mössbauer spectroscopy: isomer shifts (I.S.) of 2.90, 3.01 mm sec^{-1} are in the range associated with tin(II) species; quadrupole splittings (Q.S.) of 2.17, 1.87 mm sec^{-1} suggest considerable deviation from cubic symmetry consistent with the stereochemical influence of a non-bonding electron pair at the tin atom. Accordingly, with $BF_3 \cdot Et_2O$ compound (I) afforded an adduct (I.S. 3.77 mm sec^{-1}) demonstrating its ability to function as a Lewis base. Furthermore, treatment of compound (I) with either di-iodine or methyl iodide gives $Sn(trop)_2(X)I$ (X = I or Me) for which Mössbauer I.S. near 0.8 mm sec^{-1} confirm that these reactions constitute oxidative addition from Sn(II) to Sn(IV). Reactions of compounds (I) and (II) with $SnCl_2$ yield volatile monochloro derivatives Sn(Chel)Cl as cream powders with quadrupole split ^{119m}Sn Mössbauer resonances above

TABLE I. Physical and Analytical Data.

Compound[a]	Colour	M.P. (°C)	Calc.		Found		M		ν(C=O) (cm^{-1})
			C	H	C	H	Calc.	Found	
(I) $Sn(trop)_2$	Yellow	163–165 dec.	46.57	2.77	46.23	2.91	360	365[b]	1587vs, 1565m
(II) $Sn(thuj)_2$	Bright Yellow	107–109 dec.	54.0	4.94	55.28	5.23	445	438[c]	1587s, 1569s
(III) $Pb(trop)_2$	Yellow	230–232[d]	37.41	2.25	37.38	2.41	449	506[b,e]	1588vs, 1561vw
(IV) $Pb(thuj)_2$	Yellow	202 dec.	45.01	4.16	44.17	4.09	534	581[b]	1584vs, 1579m

[a] trop = tropolonato$^-$; thuj = β-thujaplicinato$^-$. [b] Osmometrically in chloroform solution. [c] In benzene solution. [d] *Cf.* Ref. 5. [e] In Ref. 5 this compound has been reported to be dimeric in CH_2Cl_2 solution.

3.0 mm sec^{-1}; mass spectroscopy indicates that these species are also monomeric in the vapour phase.

The ^{13}C n.m.r. spectra of compounds (I) - (IV) recorded at ambient temperature show for the C_3–C_7 ring carbon atoms an a_2b_2c structure for (I) and (III) replaced by an $aa'bb'c$ pattern in (II) and (IV) with no further splittings attributable to stereochemical non-equivalence of the chelating ligands. The dynamic characteristics[1] of the metal–chelate linkages in these species is presently being investigated using variable temperature ^{13}C as well as ^{1}H n.m.r. spectroscopy.

Acknowledgement

We thank the N. Ireland Department of Education for financial support (A.R.).

References

1 S. S. Eaton, G. R. Eaton, R. H. Holm and E. L. Muetterties, *J. Am. Chem. Soc.*, *95*, 1116 (1973) and references therein.

2 T. J. Marks and A. R. Newman, *J. Am. Chem. Soc.*, *95*, 769 (1973).

3 K. D. Bos, H. A. Budding, E. J. Bulten and J. G. Noltes, *Inorg. Nucl. Chem. Lett.*, *9*, 961 (1973); K. D. Bos, E. J. Bulten and J. G. Noltes, *J. Organometal. Chem.*, *67*, C13 (1974); P. F. R. Ewings, D. E. Fenton and P. G. Harrison, *J.C.S. Dalton*, 821 (1975).

4 J. D. Cotton, P. J. Davidson, D. E. Goldberg, M. F. Lappert and K. M. Thomas, *J.C.S. Chem. Comm.*, 893 (1974); D. H. Harris and M. F. Lappert, *ibid.*, 895 (1974).

5 E. L. Muetterties, H. Roesky and C. M. Wright, *J. Am. Chem. Soc.*, *88*, 4856 (1966).

6 L. D. Dave, D. F. Evans and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959); P. G. Harrison and S. R. Stobart, *J.C.S. Dalton*, 940 (1973).

Note added in press (November 26, 1975)

Dr. Hobart's present address is: Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2.