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Preliminary communication

ADDUCTS OF ORGANOLEAD(IV) AND ORGANOTHALLIUM(III) CHLORIDES WITH *N,N'*-ETHYLENEBIS(SALICYLIDENEIMINATO)-NICKEL(II) AND BIS(β-MERCAPTOETHYLAMINE)NICKEL(II)

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Summary

Novel 1/1 adducts of organolead(IV) and organothallium(III) chlorides with the complexes *N,N'*-ethylenebis(salicylideneiminato)nickel(II) and bis-(β-mercaptoethylamine)nickel(II) have been synthesized. Their configurations have been investigated in the solid state by IR and electronic spectroscopy and by magnetic measurements.

Introduction

The complex *N,N'*-ethylenebis(salicylideneiminato)nickel(II) [NiSalen] reacts with metal ions or R_nSnCl_{4-n} compounds to give adducts in which NiSalen acts as a bidentate neutral ligand through OO donor atoms [1]. Similar behaviour has been observed for the complex bis(β-mercaptoethylamine)-nickel(II) [$Ni(MEA)_2$] [2], which can coordinate to transition metals through SS donor atoms [3].

We describe below a comparative study of the interaction of NiSalen and $Ni(MEA)_2$ with organolead(IV) and organothallium(III) chlorides.

Experimental

The compounds $PhTlCl_2$ and Me_2PbCl_2 were made by published methods [4, 5]. Ph_2PbCl_2 was an Alfa Inorganics product.

The complex NiSalen and its adducts with Ph_2PbCl_2 and $PhTlCl_2$ were synthesized by published methods [1], using dry methanol as solvent. The complex $Ni(MEA)_2$ was prepared as previously described [2].

The adducts $Me_2PbCl_2 \cdot Ni(MEA)_2$ and $PhTlCl_2 \cdot Ni(MEA)_2$ were prepared by refluxing a methanol suspension of $Ni(MEA)_2$ (2 mmol in 50 ml) under N_2 with a methanolic solution of the organometal chloride (2 mmol in 50 ml). The

TABLE 1

MELTING POINTS AND ANALYTICAL DATA [FOUND (CALCD.) (%)]

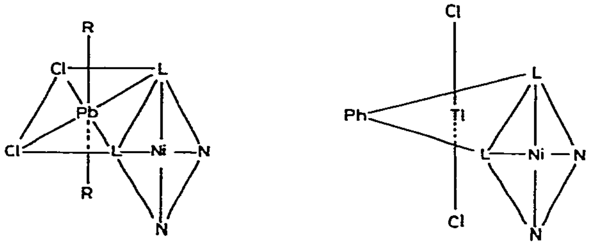
Compound (colour)	m.p. (°C)	C	H	N	S	Cl	Ni	M (Pb, Tl)
$Ph_2PbCl_2 \cdot$ NiSalen	260° dec.	44 16	3.03	3.80		9.10	8.13	27.50
(red)		(44.33)	(3.16)	(3.69)		(9.23)	(8.06)	(27.31)
$PhTlCl_2 \cdot$ NiSalen	176—178° dec.	39.11	2.83	4.08		10.60	8.89	29.86
(red)		(38.99)	(2.70)	(4.13)		(10.34)	(8.98)	(30.13)
$Me_2PbCl_2 \cdot Ni(MEA)_2$	242—243° dec.	13.90	3.60	5.22	12.61	13.67	11.40	39.59
(brown)		(13.87)	(3.47)	(5.27)	(12.33)	(13.49)	(11.69)	(39.88)
$PhTlCl_2 \cdot Ni(MEA)_2$	193—195° dec.	21.20	2.96	4.82	11.39	12.68	10.95	36.01
(pale yellow)		(21.31)	(3.02)	(4.87)	(11.36)	(12.43)	(10.78)	(36.23)

solid adducts separated on cooling, and were dried and stored under vacuum.

Analytical data are shown in Table 1. The infrared spectra were recorded with a Beckman IR 12 spectrometer, in the 4000—200 cm^{-1} region, on Nujol and hexachlorobutadiene mulls, between CsI windows. The electronic spectra in the solid state (diffuse reflectance, blank MgO) and in DMSO solution (concentration ranging from 5×10^{-6} to 1×10^{-4} M, using 1 cm optical path cells) were recorded with a Beckman DK-2A spectrophotometer. Magnetic measurements were made at room temperature by the Gouy method.

Discussion

The analytical data for all the adducts are consistent with 1/1 ligand—organometal chloride stoichiometries. The maintainance of the square planar configuration of bound NiSalen [6] and $Ni(MEA)_2$ [2] in all adducts is demonstrated by their diamagnetism as well as the coincidence of the solid state electronic spectra of free and coordinated ligands (maxima around 408 nm, shoulders at 450 and 550 nm for NiSalen and its adducts; maxima around 394 nm for $Ni(MEA)_2$ and its adducts). The infrared spectra of free NiSalen and $Ni(MEA)_2$ do not differ substantially from those of the respective adducts apart from characteristic bands involving the organic moieties bound to the metal, the metal—ligand and the metal—chloride vibrations. The bands at 450 s cm^{-1} in $Ph_2PbCl_2 \cdot$ NiSalen and at 460 m cm^{-1} in $PhTlCl_2 \cdot Ni(MEA)_2$ adducts are ascribable to the metal—phenyl y-mode in Whiffen's notation [7, 8]. No band attributable to thallium—phenyl vibration in $PhTlCl_2 \cdot$NiSalen could be identified, owing to the presence of NiSalen bands in that region. Carbon—lead skeletal vibrations in Me_2Pb^{IV} are expected around 541—523 cm^{-1}, $\nu_{as}(PbC_2)$ [9, 10], and 460—447, $\nu_s(PbC_2)$ [10]. In $Me_2PbCl_2 \cdot Ni(MEA)_2$, the broad medium band occurring at 560 cm^{-1} may originate in an overlap of $\nu_{as}(PbC_2)$ with a band at 550 cm^{-1} present in $Ni(MEA)_2$. No bands attributable to $\nu_s(PbC_2)$ are observed in the expected range, which possibly indicates a linear CPbC skeleton. The single bands at 315 s and 320 m(bd) cm^{-1}, are assigned tentatively to (Tl—Cl) vibrations [8] respectively in $PhTlCl_2 \cdot$NiSalen and $PhTlCl_2 \cdot Ni(MEA)_2$, and this would suggest a *trans*-Cl_2 arrangement. No Pb—Cl stretchings (which probably occur below 200 cm^{-1} because of the increased ionic character of the bond upon coordination by the ligand on Pb [9, 10]) can be assigned in the spectra of $Ph_2PbCl_2 \cdot$NiSalen and $Me_2PbCl_2 \cdot (NiMEA)_2$.



I. L=O, R=Ph: Ph_2PbCl_2·NiSalen.

II. L=S, R=Me: Me_2PbCl_2·$Ni(MEA)_2$

III. L=O: $PhTlCl_2$·NiSalen.

IV. L=S: $PhTlCl_2$·$Ni(MEA)_2$

Fig. 1. Structures of R_2PbCl_2 (I, II) and $PhTlCl_2$ (III, IV) adducts.

On the basis of the discussion above as well as of the earlier analyses [1], we propose the *trans*-R_2 octahedral configurations I and II (Fig. 1) for Ph_2PbCl_2·NiSalen and Me_2PbCl_2·$Ni(MEA)_2$ adducts in the solid state, and the trigonal bipyramidal structures III and IV (Fig. 1) for $PhTlCl_2$·NiSalen and $PhTlCl_2$·$Ni(MEA)_2$, with the chlorine atoms in *trans* position [8].

Dissociation of the adducts of NiSalen in dimethylsulfoxide solution into free NiSalen and organometallic chloride can be inferred from the fact that the electronic spectra associated with the ligands identical with that of the ligand, showing maxima at 408 nm and two shoulders at 440 and 385 nm. The complex $Ni(MEA)_2$ and its adducts were not investigated in solution phase because of their low solubility in polar and non polar solvents.

Acknowledgements

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