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Synthesis and Infrared Studies of Dichlorolanthanide Complexes of Ethyl 2-(Diphenyloxophosphino)-acetates*

HSU-KUN WANG**, MING-JIE ZHANG and JI-TAO WANG

Institute of Elementoorganic Chemistry, Nankai University, Tianjin, China

Although bifunctional carbamoylphosphine oxides, $R_2P(O)CH_2CONR'_2$, have been widely studied as lanthanide and actinide extractants [1–4], little is known about $R_2P(O)CH_2COOR'$ as an anion bidentate ligand capable of bonding with metal ions through C=O and P=O oxygens. In order to examine the coordination nature of one of the anion bidentate ligands, $[Ph_2P(O)CHCOOC_2H_5]^-$, we synthesized a series of complexes, $LnPh_2P(O)CHCOOC_2H_5Cl_2 \cdot 2H_2O$, and studied their solution IR spectra.

Nakamoto and coworkers [5] found that the Ni–O stretching absorption at 452 cm^{-1} for $Ni(acac)_2$ shifted to 439 cm^{-1} for $Ni(acac)_2(pyridine)_2$. Liu and coworkers [6] recorded the infrared and Raman spectra for lanthanide acetylacetonate-$\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin complexes (LnTPPacac) and found that the M–O(acac) stretching absorption near 400 cm^{-1} became weaker and shifted to lower wavenumbers because of the coordination of metal ion to TPP nitrogens. So, by the study of the solution IR spectra of our complexes, one would be able to find the difference in coordination between C=O and P=O to the metal ion.

Experimental

Syntheses

The preparation of $Ph_2P(O)CH_2COOC_2H_5$ was achieved according to the literature method [7]. The complexes $LnPh_2P(O)CHCOOC_2H_5Cl_2 \cdot 2H_2O$ were prepared by the reaction of $NaPh_2P(O)CHCOOC_2H_5$ with $LnCl_3$ in alcohol at room temperature under nitrogen. These complexes (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Ho, Er, and Y) were purified by recrystallization from CH_2Cl_2–petroleum ether. They are soluble in methanol, ethanol and dichloromethane; some of them are soluble in acetonitrile and DMSO, they decompose in air at about 100 °C.

Complexes $Ln(CH_3O)_2P(O)CHCOOC_2H_5Cl_2 \cdot nH_2O$ (Ln = Sm, Gd, Tb, and Ho) and $Y(CH_3O)_2P(O)CHCOOC_2H_5Cl_2 \cdot 2H_2O \cdot (HCONMe_2)_2$ were also prepared.

All the complexes were characterized by elemental analysis, ^1H NMR and IR. The elemental analyses table is available (see 'Supplementary Material').

Measurements

Elemental analyses were performed at the Analytical Laboratory, Institute of Elementoorganic Chemistry. ^1H NMR spectra were obtained with a JEOL FT FX-90Q NMR spectrometer in DMSO-d_6 with TMS as internal standard. IR spectra were recorded on a Nicolet FT-IR 5DX spectrometer.

Results and Discussion

Typical IR spectra are found for $Ph_2P(O)CH_2COOC_2H_5$, $SmPh_2P(O)CHCOOC_2H_5Cl_2 \cdot 2H_2O$, $(CH_3O)_2P(O)CH_2COOC_2H_5$ and $Sm(CH_3O)_2P(O)CHCOOC_2H_5Cl_2 \cdot 4H_2O$ (see 'Supplementary Material').

The ν(C=O) and ν(P=O) bands for $Ph_2P(O)CH_2COOC_2H_5$ occur at 1733 and 1265 cm^{-1}, respectively [8]. For $LnPh_2P(O)CHCOOC_2H_5Cl_2 \cdot 2H_2O$ these two bands disappear and two new absorption bands at 1590–1599 and 1160–1165 cm^{-1} emerge. These two new bands are sensitive to solvent effects and should correspond to the stretching vibrations of C=O and P=O which are strong polar bonds [9]. Also, a medium and broad band at 1381–1388 cm^{-1} should be assigned to ν(C=C). $(CH_3O)_2P(O)CH_2COOC_2H_5$ gives ν(C=O) at 1737 and ν(P=O) at 1274 cm^{-1}, but $Ln(CH_3O)_2P(O)CHCOOC_2H_5Cl_2 \cdot nH_2O$ shows these absorptions at 1580–1590 and 1170–1181 cm^{-1}. At the same time, a medium and broad absorption band at 1382–1401 cm^{-1} should be assigned to ν(C=C) [10]. The shifts of ν(C=O) and ν(P=O) can be considered as verification for the coordination of ligand C=O and P=O to the lanthanide ion, giving a six-membered ring structure.

The solution IR spectra for $LnPh_2P(O)CHCOOC_2H_5Cl_2 \cdot 2H_2O$ (Ln = Nd, Sm, Gd, Tb, Ho and Er) have been recorded and the corresponding absorption frequencies are listed in Table I.

DMSO can give strong coordination bonding to lanthanide ions through the S=O oxygen; CH_3CN does the same through the C≡N group, which is much weaker than DMSO; but CH_2Cl_2 cannot coordinate to metal ions and only gives a very weak association with ions. The ν(C=O) band for $Ph_2P(O)CH_2COOC_2H_5$ is in the order: CH_3CN (1734 cm^{-1}) > CH_2Cl_2 (1731 cm^{-1}) > DMSO (1728 cm^{-1}), which reflects the interaction between C=O and solvents. The

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**Author to whom correspondence should be addressed.

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TABLE I. ν(C=O) and ν(P=O) Values for $LnPh_2P(O)CHCOOC_2H_5Cl_2\cdot 2H_2O$ in Solution (cm^{-1})

Ln	C=O				P=O			
	DMSO	CH_3CN	CH_2Cl_2	KBr	DMSO	CH_3CN	CH_2Cl_2	KBr
Nd	1597	1592	1591	1590	1161	1161	1166	1160
Sm	1598	1594	1592	1591	1162	1162	1165	1162
Gd	1598	1593	1591	1590	1165	1164	1168	1165
Tb	1598	1594	1592	1591	1165	1165	1168	1164
Ho	1600	1595	1593	1597	1165	1165	1168	1165
Er	1600	1595	1593	1597	1164	1163	1167	1165

ν(P=O) absorption bands cannot be observed because of overlap with solvent bands. Complexes $LnPh_2P(O)CHCOOC_2H_5Cl_2\cdot 2H_2O$ in solution give the ν(C=O) order as: DMSO (Sm, 1598 cm^{-1}) > CH_3CN (Sm, 1594 cm^{-1}) > CH_2Cl_2 (Sm, 1592 cm^{-1}), since the coordination of solvent-to-metal-ion weakens the carbonyl–metal bonding. This order is consistent with the coordination ability of these solvents; the stronger the coordination, the more the reduction of carbonyl–metal bonding, and the more the shift of ν(C=O) to lower wave numbers.

The order of ν(P=O) is CH_2Cl_2 (Sm, 1165 cm^{-1}) > DMSO (Sm, 1161 cm^{-1}) ≈ CH_3CN (Sm, 1161 cm^{-1}), which is not consistent with the solvent-to-metal-ion coordination ability. So, the solvent-to-metal-ion coordination mainly weakens the carbonyl–metal bonding but not the P=O-to-metal bonding, which is much stronger.

Supplementary Material

Available from the authors on request, including Tables of elemental analyses of $LnPh_2P(O)CHCOOC_2H_5Cl_2\cdot nH_2O$, IR spectra (KBr) of $Ph_2P(O)CH_2COOC_2H_5$, $SmPh_2P(O)CHCOOC_2H_5Cl_2\cdot 2H_2O$, $(CH_3O)_2P(O)CH_2COOC_2H_5$ and $Sm(CH_3O)_2P(O)CHCOOC_2H_5Cl_2\cdot 4H_2O$.

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