ISSN 0027-1314, Moscow University Chemistry Bulletin, 2007, Vol. 62, No. 4, pp. 226–229. © Allerton Press, Inc., 2007.
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Solution and Gas-Phase Synthesis of the Heteroligand Yttrium Complex with Dipivaloylmethane and Bis(salicylidene)ethylenediamine Y(dpm)(salen)

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Received September 4, 2006

Abstract—The interaction of yttrium dipivaloylmethanate Y(dpm)$_3$ with bis(salicylidene)ethylenediamine (H$_2$salen) in solution and the gas phase leads to the formation of the heteroligand complex Y(dpm)(salen). The composition of the product has been confirmed by IR spectroscopy, ^{1}H NMR, and elemental analysis. The introduction of a Schiff base excess into the solution or gas phase does not result in the formation of the homoleptic complex Y$_2$(salen)$_3$.

DOI: 10.3103/S0027131407040116

Rare earth complexes have some interesting functional properties (magnetic, optical, etc.); therefore, they are candidates for use in the form of thin films in different devices with a planar structure. In particular, some rare earth β-diketonates, pyrazolonates, and aromatic carboxylates exhibit luminescent properties and can be used as emitting layers in organic electroluminescent devices (OLEDs) [1–3]. The performance of these devices depends on many factors, one of which is the quality of the resulting film. Chemical vapor deposition of a compound on a substrate ensures higher quality films [4]; however, the method requires volatile compounds. Most rare earth β-diketonates and pyrazolonates are volatile, whereas aromatic carboxylates and some other rare earth complexes, such as complexes with Schiff bases, are nonvolatile. These rare earth complexes are of interest as magnetic and luminescent materials [5, 6].

Exchange reactions of rare earth β diketonates with carboxylic acids [7] lead to the formation of tris-carboxylates:

$$\mathrm{Ln(dik)_3 + 3HL \longrightarrow LnL_3 + 3Hdik}, \qquad (1)$$

where Hdik is a β-diketone, Ln is a lanthanide, and HL is a carboxylic acid.

Such reactions occur in solution. The equilibrium of reaction (1) is shifted to the right due to the difference in acidity between β-diketonates and carboxylic acids, as well as due to different solubilities of the reagents and products.

The interaction of Ln(dpm)$_3$ (Hdpm is dipivaloylmethane) with benzoic acid exemplifies the possibility of the gas-phase variant of reaction (1) [8]. In this case, the shift of equilibrium to the right is due to the different volatilities of β-diketonates and carboxylates [9]. This procedure was used to obtain thin films of rare earth benzoates [10]. Thus, the gas-phase reaction holds promise for the synthesis of a wide range of thin-film materials.

In this work, we have considered whether the gas-phase reaction (1) between volatile rare earth β-diketonates and Schiff bases is possible.

The objects of investigation were H$_2$salen, a Schiff base (the derivative of salicylaldehyde and ethylenediamine), and yttrium dipivaloylmethanate Y(dpm)$_3$ since this compound is volatile, thermally stable, and mononuclear in the gas phase; in addition, for this compound, the saturated vapor pressures as a function of temperature are known [11]. The choice of yttrium among the rare earth elements is caused by the possibility to use ^{1}H NMR for identification of the reaction products.

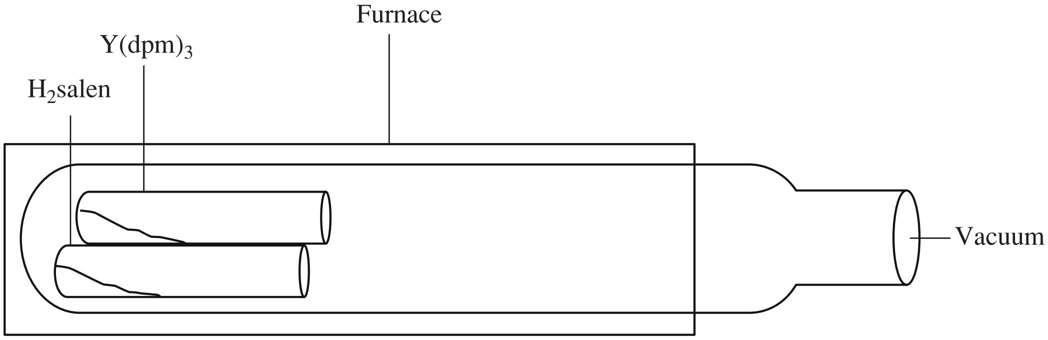
EXPERIMENTAL

Reagents

Ethylenediamine (NH$_2$)$_2$C$_2$H$_4$ (Aldrich), dipivaloylmethane Hdpm (Fluka), yttrium nitrate Y(NO$_3$)$_3$ · 4H$_2$O (pure for analysis), sodium hydroxide NaOH (pure for analysis), ethanol (pure grade), and benzene C$_6$H$_6$ (pure for analysis) were used. Salicylaldehyde C$_6$H$_4$(OH)CHO was purified by vacuum distillation (T_b = 93°C/25 mmHg).

Methods of Investigation

The content of Y(III) in the complexes was determined by complexometric titration (the accuracy of determination, ±0.2%) [12].



Horizontal vacuum reactor.

The content of carbon, hydrogen, and nitrogen was determined by elemental microanalysis on a TsKhLS-BNIKhFI CHN analyzer.

The IR spectra of the complexes were recorded as KBr discs on a PE-FTIR-1600 spectrophotometer in the range 7000–400 cm^{-1}.

The ^1H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz).

Synthesis

Synthesis of $Y(dpm)_3$. $Y(dpm)_3 \cdot 2H_2O$ was synthesized as described in [11]. Anhydrous $Y(dpm)_3$ was obtained by sublimation of the hydrated complex in vacuo (0.01 mmHg) at 120–150°C. The yield was ~80%.

For $C_{33}H_{57}O_6Y$ anal. calcd. (%): C, 62.1; H, 8.9; Y, 13.9. Found (%): C, 61.9; H, 9.0; Y, 14.0.

Synthesis of H_2salen was carried out as described in [13] by condensation of 10 mmol of $(NH_2)_2C_2H_4$ with a stoichiometric amount of aldehyde in alcohol upon heating under reflux. The product was filtered off and dried in air. Yield, ~90%.

^1H NMR (δ, ppm, DMSO/TMS): 13.20 (s, 2H), 8.33 (s, 2H), 7.28 (d, 2H), 7.21 (s, 2H), 6.93 (d, 2H), 6.84 (d, 2H), 3.90 (s, 4H).

Reaction of $Y(dpm)_3$ with H_2salen. The reaction was carried out in benzene at the reagent ratio 1 : 1.5 and 1 : 2 as follows: To a hot solution of 1.5 mmol (or 2 mmol) of H_2salen in benzene (5 mL), a solution of 1 mmol of $Y(dpm)_3$ in benzene (5 mL) was added. The resulting reaction mixture was heated under continuous stirring until the formation of a precipitate, which was filtered off and dried in vacuo for 30 min at 60–80°C (0.01 mmHg).

The composition of the product at the reagent ratio 1 : 1.5. For $YC_{27}H_{33}N_2O_4$ anal. calcd. (%): C, 60.2; H, 6.5; N, 5.2. Found (%): C, 60.3; H, 6.5; N, 5.2.

IR (cm^{-1}): 3055, 3023, 1627, 1640 sh (C=N), 1599 (C=O), 1578 (N–H), 1556 (C=O), 1540 (C=O).

^1H NMR (δ, ppm, DMSO/TMS): 8.32 (s, 2H), 8.06 (d, 2H), 7.20 (d, 2H), 6.93 (d, 2H), 6.81 (d, 2H), 5.61 (m, 1H), 1.14 (d, 18H).

The composition of the product at the reagent ratio 1 : 2. For $YC_{27}H_{33}N_2O_4$ anal. calcd. (%): Y, 16.5; C, 60.2; H, 6.5; N, 5.2. Found (%): Y, 16.3; C, 60.1; H, 6.5; N, 5.4.

IR (cm^{-1}): 3056, 3023, 1629, 1640 sh (C=N), 1600 (C=O), 1578 (N–H), 1556 (C=O), 1541 (C=O).

^1H NMR (δ, ppm, DMSO/TMS): 8.26 (s, 2H), 8.06 (d, 2H), 7.20 (d, 2H), 6.93 (d, 2H), 6.81 (d, 2H), 5.61 (m, 1H), 1.14 (d, 18H).

Reaction of $Y(dpm)_3$ with H_2salen in the gas phase. The synthesis was carried out in a horizontal vacuum reactor (figure) at a pressure of 0.01 mmHg. The construction of the reactor ensured the interaction of reagent vapors in the hot zone of the reactor since the evaporators were mounted at the same level. The product was deposited on the walls of the hot zone of the reactor. The synthesis was carried out at 180–200 and 250°C for 60 min.

The composition of the product obtained at 180–200°C. IR (cm^{-1}): 3061, 3048, 1629, 1640 sh (C=N), 1598 (C=O), 1578 (N–H), 1556 (C=O), 1540 (C=O).

^1H NMR (δ, ppm, DMSO/TMS): 8.26 (s, 2H), 8.05 (d, 2H), 7.20 (d, 2H), 6.93 (d, 2H), 6.83 (d, 2H), 5.60 (m, 1H), 1.14 (d, 1H).

The composition of the product obtained at 250°C. IR (cm^{-1}): 3061, 3048, 1628, 1640 sh (C=N), 1598 (C=O), 1578 (N–H), 1557 (C=O), 1541 (C=O).

^1H NMR (δ, ppm, DMSO/TMS): 8.26 (s, 2H), 8.05 (d, 2H), 7.20 (d, 2H), 6.93 (d, 2H), 6.83 (d, 2H), 5.60 (m, 1H), 1.14 (d, 1H).

RESULTS AND DISCUSSION

As shown in [14], the exchange reaction between rare earth β-diketonates and H_2salen leads to the formation of partially substituted products, and their composition depends on the nature of the β-diketonate: $Ln(dik)_2(salen)_{0.5}$ (dik is acetylacetone, propionylacetone) and Ln(dik)(salen) (dik is benzoylacetone, dibenzoylmethane). However, such a reaction have not been described for dipivaloylmethanates. Therefore, we studied the reaction of $Y(dpm)_3$ with H_2salen in solution and in the gas phase.

The interaction of $Y(dpm)_3$ with H_2salen (reaction (2)) was carried out in benzene since the reagents are readily soluble in this solvent. The reaction was carried out with a stoichiometric amount of H_2salen (for the formation of $Y_2(salen)_3$, $n = 3$), as well as with its excess.

$$\begin{gathered}Y(dpm)_3 + n/2\ H_2salen \\ \longrightarrow Y(dpm)_{3-n}(salen)_{n/2} + nHdpm.\end{gathered} \tag{2}$$

In both cases, the reaction yielded the precipitates of the heteroligand complex Y(dpm)(salen) as determined by elemental analysis and IR and ^{1}H NMR spectroscopy. The variation of the reagent ratio did not change the composition of the product, which is evidence of the formation of an individual heteroligand complex.

The IR spectra of the complexes show the stretching vibration bands ν(C=O) (1598, 1556 cm^{-1}) and ν(C–C) (1540 cm^{-1}) typical of the dipivaloylmethanate ligand, as well as ν(C=N) (1629 cm^{-1}) and δ(N–H) (1578 cm^{-1}) typical of the Schiff base. In addition, the range of ν(C–H) stretching vibrations in the spectrum of the heteroligand complex shows not only the bands typical of the methyl groups of the dipivaloylmethanate ligand, but also higher frequency vibrations caused by the presence of the $salen^{2-}$ ligand.

The signals of both ligands dpm^- and $salen^{2-}$ were observed in the ^{1}H NMR spectrum of the complex. Their integrated intensity ratio corresponded to the ligand ratio in the complex: $[dpm^-] : [salen^{2-}] = 1 : 1$.

Conditions for the gas-phase reaction were chosen according to the temperature dependences of $Y(dpm)_3$ and H_2salen saturated vapor pressures. The temperature dependence of saturated vapor pressure is known for $Y(dpm)_3$ [11]; however, no such data are available for H_2salen. To estimate the thermodynamic parameters of H_2salen evaporation, the temperature dependences of saturated vapor pressures of related aromatic compounds (methylbenzimidazole, phenylimidazoline, phenylbenzimidazole) [15] were examined. Inasmuch as the thermodynamic parameters of evaporation are close in this series (for the equation $\log p = A - B/T$, the A values are within 12.64–15 and the B values are within 5305–7313), we assumed that for the vapor pressure for H_2salen differs slightly from the known pressures and can be obtained by averaging these data:

$$H_2salen\text{: } \log p = 14 - 6000/T, \quad T = 436\text{–}466\ K,$$

$$Y(dpm)_3\text{: } \log p = 15.799 - 7388.6/T, \quad T = 420\text{–}454\ K.$$

It follows from these dependences that the ratio of the saturated vapor pressures $p(H_2salen) : p(Y(dpm)_3$ decreases with an increase in temperature, whereas the reactivity increases. Two gas-phase syntheses were carried out under different conditions. In the first experiment, the temperature was chosen such that the vapor pressure ratio $p(Y(dpm)_3) : p(H_2salen)$ in the gas phase was close to the stoichiometry of the reaction, 1.0 : 1.5 ($T = 250°C$). The second experiment was carried out at a lower temperature, which increases the partial pressure of H_2salen (T = 180–200°C, $p(Y(dpm)_3) : p(H_2salen) = 1.0 : 2.5$). In both experiments, the reaction led to the deposition of the product in the hot zone of the reactor in low yield.

The formation of the nonvolatile product in the hot zone of the reactor is indirect evidence that reaction (2) occurs since, as distinct from the probable product, the initial reagents go into the gas phase at the experimental temperatures.

The IR and ^{1}H NMR data on the products obtained and their comparison with the elemental analysis data for the complex Y(dpm)(salen) obtained in solution show that both gas-phase experiments lead to the same complex Y(dpm)(salen).

Thus, reaction (2) occurs in both the solution and gas phase to produce the heteroligand complex Y(dpm)(salen). Even in the presence of an H_2salen excess, $salen^{2-}$ does not completely substitute for the dpm^- ligand. This is likely due to the fact that the Y(dpm)(salen) complex is insoluble in benzene and nonvolatile; i.e., it escapes from the reaction zone. However, it is precisely this fact that leads to the occurrence of reaction (2) since H_2salen is a weaker acid than Hdpm. Therefore, if the heteroligand complex were not removed from the reaction zone, the equilibrium of reaction (2) would not be shifted to the right. The fact that reaction (2) occurs in the gas phase to yield the nonvolatile heteroligand complex gives grounds to expect that reactions of this type may be used for producing films of nonvolatile rare earth complexes with Shiff bases.

REFERENCES

1. Kido, J. and Okamoto, Y., *Chem. Rev.*, 2002, vol. 102, no. 6, p. 2357.
2. Kuz'mina, N.P. and Eliseeva, S.V., *Zh. Neorg. Khim.*, 2006, vol. 51, no. 1, p. 80.
3. Katkova, M.A., Vitukhnovskii, A.G., and Bochkarev, M.N., *Usp. Khim.*, 2005, vol. 74, p. 1193.
4. Kaul', A.R., *Zh. Vses. Khim. O-va im. D.I. Mendeleeva*, 1989, vol. 34, no. 4, p. 492.
5. Costes, J.-P., *Inorg. Chim. Acta*, 1998, vol. 268, no. 1, p. 125.
6. Gaiduk, M.I., Zolin, V.F., and Gaigerova, L.S., in *Spektry lyuminestsentsii evropiya* (Luminescence Spectra of Europium), Moscow, 1974, p. 195.

7. Kuz'mina, N.P., An' Tu Zoan, Pisarevskii, A.P., Martynenko, L.I., and Struchkov, Yu.T., *Koord. Khim.*, 1994, vol. 20, p. 707.
8. Kuz'mina, N.P., Fenkhua Lyu, and Martynenko, L.I., *Koord. Khim.*, 1998, vol. 24, p. 363.
9. Kotova, O., Eliseeva, S., Muydinov, R., Kuzmina, N., and Kaul, A., *Electrochem. Soc. Proc. PV*, 2005, no. 9, p. 306.
10. Kuzmina, N., Martynenko, L., Chugarov, N., Zaitseva, I., Grigoriev, A., and Yakushevich, A., *J. Alloys Comp.*, 2000, no. 308, p. 158.
11. Eisentraut, K.J. and Sievers, R.E., *J. Am. Chem. Soc.*, 1965, vol. 87, p. 5254.
12. Přibil, R., *Kompleksony v khimicheskom analize* (Complexones in Chemical Analysis), Moscow, 1955, p. 187.
13. Pereira, E., Gomes, L., and de Castro, B., *Inorg. Chim. Acta*, 1961, vol. 14, p. 147.
14. Dutt, N.K. and Nag, K., *J. Inorg. Nucl. Chem.*, 1968, vol. 30, p. 2779.
15. Lebedev, Yu.A. and Miroshnichenko, E.A., *Termokhimiya paroobrazovaniya organicheskikh veshchestv* (Thermochemistry of Vaporization of Organic Compounds), Moscow, 1981, p. 146.