Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Solid State Preparation of the (8-Hydroxyquinolinato)Aluminum(Iii) Complex from Aluminum Isopropoxide and 8-Hydroxyquinoline

A. K. Saxena [a]

[a] Department of Physics & Astrophysics , University of Delhi , Delhi, 110007, India

To cite this article: A. K. Saxena (1999) Solid State Preparation of the (8-Hydroxyquinolinato)Aluminum(Iii) Complex from Aluminum Isopropoxide and 8-Hydroxyquinoline, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 29:10, 1747-1767, DOI: 10.1080/00945719909351733

To link to this article: http://dx.doi.org/10.1080/00945719909351733

SYNTH. REACT. INORG. MET.-ORG. CHEM., 29(10), 1747–1767 (1999)

SOLID STATE PREPARATION OF THE (8-HYDROXYQUINOLINATO)ALUMINUM(III) COMPLEX FROM ALUMINUM ISOPROPOXIDE AND 8-HYDROXYQUINOLINE

A. K. Saxena
Department of Physics & Astrophysics
University of Delhi, Delhi-110007, India

ABSTRACT

A new alternate method is described for the preparation of the (8-hydroxyquinolinato)aluminum(III) complex in the solid state from aluminum isopropoxide. The complex was characterised by IR spectra, elemental analyses and X-ray spectroscopy using a compact X-ray diffraction analyser. The light yellow complex prepared in the solid state has an identical structure with the one prepared by the wet method.

INTRODUCTION

The use of 8-hydroxyquinoline for the precipitation of a number of metals is a well established procedure. 8-Hydroxyquinoline was introduced as an analytical reagent by Hahn[1] and Berg[2] in 1926-27 and it has since been proven to be one of the remarkable and important analytical reagents up to this time.

Extensive work[3,4] on metal complexes with oxine has been carried out earlier to determine various physico-chemical characteristics along with structural studies by X-ray diffraction and IR spectra. Although metal alkoxides have been known for many years and used in a number of organic reactions, it is surprising how few systematic studies regarding their properties have been carried out on individual compounds.

It is well known that aluminum isopropoxide exists in at least two different forms. Molecular weight determinations[5] have shown that in benzene solution the ‘aged’ solid is tetrameric while freshly distilled isopropoxide is trimeric. ^{1}H NMR spectroscopy[6] fully supports two different structures for the tetramer and trimer. Solubility studies have shown that the trimer is highly soluble in pyridine while the tetramer is only slightly soluble in this solvent. Generally, commercial aluminum isopropoxide is distilled *in vacuo* at a fixed temperature using a conventional apparatus.

It is well known that aluminum compounds, like those of cadmium, give a strong yellow fluorescence[7] when treated with 8-hydroxyquinoline. Light-emitting diodes (LEDs) based on organic multiple quantum wells (MQWs) are of much interest for use in modern electronic devices. Organic LEDs with MQW structures are expected to have narrow spectral emission, good emission efficiency and even a tunable emission spectrum. However, the properties of these structures depend strongly on the uniformity, interfacial roughness and coherence throughout the entire stack. In particular, the large-area uniformity of these structures in organic electroluminescent diodes is crucial for their application to large-area displays. Besides, both the optical and the electronic properties are governed by the nature of excitons in the organic semiconductor. Thus, the fabrication of high-quality organic MQW structures and the investigation of exciton confinement in these structures by determining their optical properties is very important. This is also the basis and key for application of organic MQW structures in LED devices.

Recently, Shiyong Liu et al.[8] prepared high-quality organic multiple quantum well (MQW) structures based on (8-hydroxyquinilato)Al(III) and 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadizole (PBD) by using a multisource-type high-vacuum organic molecular beam deposition system. Small-angle X-ray diffraction measurements confirmed that the above MQW structures have a very uniform layered structure throughout the entire stack. Both optical absorption and photoluminescence measurements revealed the evidence for exciton confinement in the (8-hydroxyquinolinato)Al(III)/PBD MQW structures. The thickness-dependent blue-shift of the photoluminescence peak observed upon decreasing the well width was attributed to the change of exciton energy as a result of quantum confinement. Theoretical calculations were also performed by

Shiyong Liu et al.[8] and they found that their results tallied with the experimental results.

Chirnside et al.[9] precipitated aluminum quantitatively by oxine and studied the structure of the complex by X-ray diffraction. His results showed that the aluminum complex was obtained in the anhydrous form by drying at 98°C and that there was no particular advantage, save that of speed, in drying at higher temperatures. The X-ray patterns confirmed that no change of phase takes place between 98° and 160°C.

Chirnside et al.[9] prepared the (8-hydroxyquinolinato)aluminum(III) complex from an aluminum salt. They took 5.5668 g, (14.8 mmole) aluminum nitrate and dissolved it in 1N hydrochloric acid (150 mL). In this solution 5 g, (64.9 mmole) of ammonium acetate was added and the solution was made alkaline by ammonia using bromocresal purple as indicator. A 2% oxine solution in 2N acetic acid was added to it slowly. The solution was stirred briskly during the addition and later on it was heated to boiling. After cooling it to room temperature the resulting precipitate was filtered and washed several times with hot water and finally with cold water and dried at 135°C in an oven for 2 h. They analysed the complex.

RESULTS AND DISCUSSION

Aluminum isopropoxide (trimer) and 8-hydroxyqunioline were mixed as solids in the molar ratio of 1:3, respectively. This corresponds to the stoichiometry of the reaction which is as follows:

$$\mathrm{Al[OCH(CH_3)_2]_3 + 3C_9H_7NO \longrightarrow Al[C_9H_6NO]_3 + 3(CH_3)_2CHOH}$$

The mixture initially was at room temperature and as the temperature of the oven was gradually increased to 60°C, the yellow colour of the mixture also intensified and no melting of the mixture was observed. However at 70°C a light brown thin ring around the inside edge of china clay dish was observed which may be due to unreacted 8-hydroxyqunioline and this was removed. This unreacted 8-hydroxyqunioline accounts for the low yield of the complex. At the reaction temperature of 60°C isopropanol is given off as the reaction proceeds with formation of aluminum oxinate which is confirmed by the yellow fluoroscence. The difference in weight between the reactants and the products at 60°C is equivalent to the loss of isopropanol only, showing that the mobility of the constituents of the reaction mixture is negligible at this stage. The ease with which the reaction occurs, suggests that the degree of mixing the solids is not a limiting factor. This, in turn, suggests that the mobility of the reactant molecules plays a vital role. Provided that the particles of the two substances are in reasobably close proximity, reaction will occur because of the mobility of the molecules[10].

The complex was purified[11] by distilling the impure product at 145-150°C at 5 mm/Hg to remove unreacted aluminum isopropoxide and finally washing it several times with water. The experimental yield of complex was found to be 87.0%. This shows that the reaction did not go to completion. The reactants and products were subjected to X-ray powder diffraction. The X-ray powder diffraction pattern of the product obtained by this method was identical to that obtained by the wet method (Table I), Analytical results are given in Table II. IR spectra obtained for the complex as prepared by the wet method and the present dry method were also found to be identical (Table III).

EXPERIMENTAL

Materials

Aluminum isopropoxide (K. Light), aluminum nitrate, 8-hydroxyquinoline, hydrochloric acid, glacial acetic acid, ammonium acetate, ammonium hydroxide, sodium hydroxide were AR, BDH (England) products. Bromocresol purple was obtained from LR BDH (England).

Synthesis

Aluminum isopropoxide (0.2043 g, 0.001 mole) and 8-hydroxyquinoline (0.4355 g, 0.003 mole) were mixed in finely powdered forms in a china clay dish. As soon as the powders were mixed at room temperature the mixture slowly started to react showing a canary-yellow fluorocence which indicated

Table I

X-ray Powder Diffraction Data

COMPOUND	$2\theta^0$	$d = \lambda/2 \sin \theta$ (λ = 1.541838)	Peak	Remark
8-Hydroxyquinoline C_9H_7NO				Definite Structure
	6.66	13.260	13.2720	
	6.76	13.064	13.0760	
	8.74	10.108	10.1170	
	9.10	9.709	9.7180	
	12.14	7.284	7.2905	
	13.88	6.374	6.3802	
	15.16	5.839	5.8443	
	18.46	4.802	4.8063	
	19.62	4.520	4.5247	
	23.12	3.843	3.8470	
	23.32	3.811	3.8145	
	23.40	3.798	3.8016	
	25.32	3.514	3.5175	
	26.84	3.318	3.3217	
	26.96	3.304	3.3072	
	27.84	3.201	3.2046	
	28.36	3.114	3.1470	
	29.66	3.009	3.0120	
	37.98	2.367	2.3691	
		and many more		

(continued)

Table I, continued

COMPOUND	$2\theta^0$	$d = \lambda/2 \sin\theta$ ($\lambda = 1.541838$)	Peak	Remark
Aluminum Isopropoxide $Al[OCH(CH_3)_2]_3$				Definite Structure
	8.42	10.497	10.5010	
	8.82	10.015	10.0260	
	8.94	9.882	9.8916	
	9.84	8.900	8.9888	
	20.56	4.310	4.3199	
	20.96	4.234	4.2383	
	21.56	4.118	4.1217	
	22.12	4.015	4.0186	
	22.30	3.985	3.9866	
	22.82	3.893	3.8969	
	24.86	3.578	3.5816	
	25.48	3.492	3.4958	
	25.64	3.421	3.4743	
	25.92	3.434	3.4375	
	26.06	3.416	3.4167	
	27.00	3.299	3.0240	
	28.64	3.114	3.1169	
	28.80	3.092	3.0999	
	29.08	3.068	3.0707	
	29.36	3.039	3.0421	
	30.06	2.920	2.9728	
	35.94	2.496	2.5001	
	37.24	2.412	2.4145	
		and many more		

Table I, continued

COMPLEX	$2\theta^0$	$d = \lambda/2 \sin\theta$ ($\lambda = 1.541838$)	Peak	Remark
	38.04	2.363	2.3655	
	63.74	1.458	1.4704	
		and many more		
Dry method				Definite
$Al[C_9H_6NO]_3$				Structure
	7.96	11.092	11.1070	
	9.20	9.604	9.6126	
	9.30	9.501	9.5095	
	10.50	8.417	8.4252	
	10.90	6.109	8.1169	
	11.18	7.907	7.9142	
	11.68	7.569	7.5765	
	12.02	7.356	7.3630	
	12.62	7.008	7.0142	
	13.88	6.374	6.3802	
	14.02	6.311	6.3168	
	14.16	6.249	6.2547	
	15.06	5.877	5.8828	
	15.26	5.801	5.8062	
	15.34	5.771	5.7761	
	15.78	5.611	5.6160	
	16.08	5.502	5.5119	
	16.76	5.285	5.2898	
	16.84	5.260	5.2648	
	17.54	5.051	5.0563	

(continued)

Table I, continued

COMPLEX	$2\theta^0$	$d = \lambda/2 \sin \theta$ (λ = 1.541838)	Peak	Remark
Dry method $Al[C_9H_6NO]_3$				Definite Structure
	17.80	4.978	4.9830	
	17.88	4.956	4.9609	
	18.68	4.746	4.7502	
	22.58	3.934	3.9378	
	23.02	3.860	3.8635	
	25.50	3.490	3.4931	
	27.18	3.278	3.2809	
	27.30	3.263	3.2667	
	28.36	3.144	3.1470	
	29.22	3.053	3.0563	
	30.68	2.911	2.9141	
	31.40	2.846	2.8489	
	31.74	2.816	2.8192	
	33.24	2.692	2.6953	
	33.60	2.664	2.6672	
	40.92	2.203	2.2054	
	44.40	2.038	2.0403	
	45.14	2.006	2.0086	
	45.56	1.989	1.9910	
	54.5	1.682	1.6837	

Table I, continued

COMPLEX	$2\theta^0$	$d = \lambda/2 \sin \theta$ (λ = 1.541838)	Peak	Remark
Wet method				Definite
$Al[C_9H_6NO]_3$				Structure
	8.00	11.100	11.0521	
	9.34	9.627	9.6335	
	9.34	9.458	9.4688	
	10.60	8.335	8.3459	
	11.00	8.040	8.0433	
	11.30	7.969	7.9711	
	11.76	7.497	7.5252	
	12.14	7.281	7.2905	
	12.60	7.019	7.0253	
	13.82	6.397	6.4170	
	14.10	6.273	6.2811	
	14.16	6.245	6.2547	
	15.02	5.867	5.8984	
	15.30	5.781	5.7911	
	15.38	5.757	5.7612	
	15.72	5.629	5.6373	
	16.00	5.530	5.5393	
	16.70	5.298	5.3086	
	16.90	5.218	5.2217	
	17.56	5.062	5.0505	
	17.74	4.985	4.9997	
	17.82	4.979	4.9830	

(continued)

Table I, continued

COMPLEX	$2\theta^0$	$d = \lambda/2 \sin \theta$ ($\lambda = 1.541838$)	Peak	Remark
Wet method $Al[C_9H_6NO]_3$				Definite Structure
	18.72	4.701	4.7401	
	22.64	3.895	3.9275	
	23.10	3.832	3.8503	
	25.48	3.491	3.4958	
	27.22	3.268	3.2762	
	27.34	3.259	3.2621	
	28.40	3.129	3.1427	
	29.20	3.050	3.0563	
	30.58	3.920	2.9234	
	31.76	2.809	2.8174	
	33.28	2.685	2.6922	
	33.58	2.660	2.6688	
	40.98	2.195	2.2023	
	45.10	2.010	2.0103	
	45.64	1.985	1.9877	
	53.95	1.790	1.7920	
	54.48	1.683	1.6843	

TABLE II

Analytical Data of (8-Hydroxyquinolinato)aluminum(III) Complex

Compound	M.p.	Found (Calc.) %					Yield %
	°C	C	H	N	O	Al	
$Al[C_9H_6NO]_3$ $AlC_{27}H_{18}N_3O_3$ (FW 459.46)							
DRY METHOD	340 (d)	70.48	3.90	9.20	10.57	5.91	87.0
		(70.52)	(3.92)	(9.14)	(10.52)	(5.87)	
WET METHOD	345	70.54	3.91	9.08	10.55	5.90	99.9

d = decomposition temperature.

Table III

IR Spectral Data of the (8-Hydroxyquinolinato)aluninum(III) Complex (cm^{-1})

DRY METHOD	WET METHOD	BAND ASSIGNMENTS
3405[a]	3400	
3046[a]	3043	C – H Stretching
1719[a]	1720	
1605[a]	1605	Aromatic C – C Multiple Bond Stretching
1580[a]	1582	-do-
1500[a]	1504	-do-
1470[a]	1472	-do-
1383[a]	1385	C – H Bending
1330[a]	1329	-do-
1282[a]	1280	C – N Stretching
1226[a]	1224	-do-
1190[a]	1191	C – O Bond
1166[a]	1164	
1115[a,c]	1111	M – O Bond
1058[a]	1052	
1033[c]	1035	
824[b]	822	C – C Stretching (Ring)
804[b]	805	C – H Rocking

Table III continued

DRY METHOD	WET METHOD	BAND ASSIGNMENTS
784[b]	780	
747[b]	748	Chelate
648[b]	649	Chelate
576[b]	578	-do-
546	544	
458[b]	460	
420	423	

Band Assignments:

(a) J. P. Phillips and J. F. Deye, Anal. Chim. Acta, 17, 231 (1957).

(b) J. C. Fanning and H. B. Jonassen, J. Inorg. Nucl. Chem, 25, 29 (1963).

(c) R. G. Charles, H. Freiser, R. Fridel, L. H. Hilliard and W. D. Johnston, Spectrochim. Acta, 8, 1 (1956).

that reaction had started at room temperature. The above mixture was kept in an oven at 60°C for 1 h and the canary-yellow fluoroscence further intensified. The temperature of the oven was then raised to 70°C and maintained at that level for 2 h.

Finally, after cooling to room temperature the product was distilled at 145-150°C at 5 mm/Hg to remove the unreacted aluminum isopropoxide present in the complex. The product was cooled again to room temperature and extracted with 100 mL double-distilled cold water. After vigorous stirring for 30 min in water, the water was decanted through a G4 Gooch crucible. This process was repeated several times to wash the complex and finally the complex was filtered. The complex was dried in a vacuum desiccator over silica gel for two days, the experimental yield was 0.4 g (87%). The aluminum in the complex was determined by a standard method[12].

Instrumentation

X-ray powder diffraction patterns were obtained on a Philips Compact X-ray diffraction analyser model P.W. 1840/04/11 with the following operating conditions: 40kV, 25 ma, slit width of 0.2 mm, copper-LFF tube, angular range 3.0° to 65.0°, scan speed $0.20^\circ 2\theta/s$ (standard default value), chart speed 20 mm $/2^\circ\theta$, chart range 1 to $1\mathrm{x}10^4$, time constant 1.0 second, nickel filter, at 20° C temperature. The IR spectra were recorded on a 200-91527 Shimadzu spectrophotometer as KBr discs. The complexes were subjected to microanalyses at the Chemistry Department, Catholic University, Nijmegen, Holland.

ACKNOWLEDGEMENT

My thanks go to the Chemistry Department of the University of Dar Es Salaam, Tanzania, for research facilities. The paper is dedicated to the memory of the late Prof. A. Steyermark of the Department of Chemistry, Rutgers University, Newark, New Jersey, USA, who was the Founding Editor of the Microchemical Journal. I am also thankful to the Council of Scientific and Industrial Research, New Delhi, India, for financial assistance and Prof. Abhai Man Singh of the Department of Physics and Astrophysics, University of Delhi, Delhi-7, for providing space for completing this work.

REFERENCES

1. F. Hahn, Z. Angew. Chem., 39, 1198 (1926).
2. R. Berg, J. Prakt. Chem., 115, 178 (1927); Chem. Abstr., 21, 1237 (1927).
3. H. Freiser, Analyst (London), 77, 830 (1952).
4. R. G. Charles, H. Freiser, R. Friedel, L. E. Hilliard and W. D. Johnston, Spectrochim. Acta, 8, 1 (1956).
5. V. J. Shiner,D. Whittaker and V. P. Fernandez, J. Am. Chem. Soc., 85, 2318 (1963).
6. I. J. Worrall, J. Chem. Educ., 46, 510 (1969).
7. F. J. Welcher, "Organic Analytical Reagents", Vol. I, D. Van Nostrand Co., Inc., New York, N.Y. p.288 (1947).
8. H. An, B. Chen, J. Hou, J. Shen and S. Liu, J. Phys. D. Appl. Phys. 31, 1148 (1998).
9. R. C. Chirnside, C. F. Pritchard and H. P. Rooksby, Analyst., 66, 399 (1941).
10. G. C. Bond, "Heterogeneous Catalysis; Principles and Applications", Second Edition, Clarendon Press, Oxford (1987).
11. W. G. Young, W. H. Hartung and F. S. Crossley, J. Am. Chem. Soc. 58, 100 (1936).

12. A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis", Third Edition (ELBS), Longman, London p. 516 (1961).

Received: 17 August 1998
Accepted: 1 July 1999

Referee I: X. R. Bu
Referee II: J. J. Alexander