

Electrochemical Synthesis and Properties of some Metal Perfluoro- β -diketdiiminates

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Introduction

The complexes of fluoro- β -diketonates have been studied for some years, because of their unique physical and chemical properties [1–3]. At the same time the simple analogues in which one or both oxygen atoms are replaced by other elements (S, N, etc.) have only recently received attention [1, 2]. While only few examples of mixed metal fluoro- β -diketdiiminates are known [4], no attempts to synthesize the real chelate of metal fluoro- β -diketdiiminate have been made although some examples of such nonfluorinated complexes do exist [5, 6]. Herein we report electrochemical synthesis and properties of some metal complexes derived from 2-amino-4-imino-perfluoropenten-2.

Results and Discussions

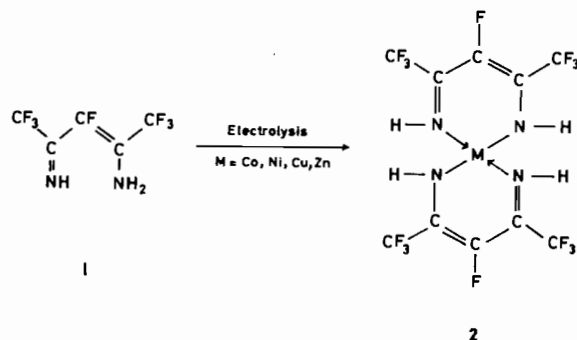
The original route for the synthesis of metal β -diketdiiminates comprises preparation of vinylogous amidinium salts from enaminketones, followed by the reaction of these salts with some inorganic metal complexes [7–9].

An application of this route for the synthesis of metal fluoro- β -diketdiiminates is not possible because of the high resistance of fluoroenaminketones towards such reactions [2]. The only opportunity to prepare a mixed chelate of platinum fluoro- β -diketdiiminate in the form of its perchlorate or tetrafluoroborate salts was reported recently as the reaction of hexaammonia-platinum tetrachloride with 1,1,1-trifluoroacetylacetone [4].

In order to avoid the above difficulties we used directly 2-amino-4-imino-perfluoropenten-2 (I) for electrochemical synthesis of metal perfluoro- β -diketdiiminates*. All protons in compound I are not too acidic (according to p.m.r. spectra, the pK value is within the range of alcohols) and due to this an electrochemical method has been chosen in particular

*The initial 2-amino-4-imino-perfluoropenten-2 can be obtained directly by the reaction of perfluoropenten-2 with ammonia gas [10].

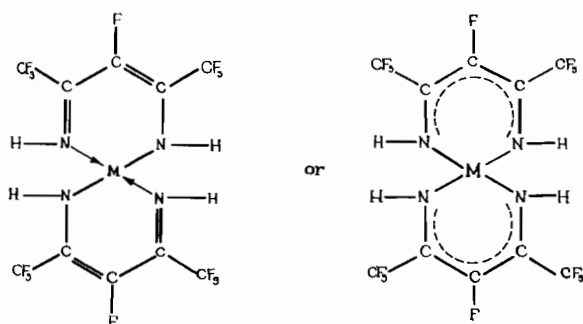
because of successful attempts for direct electrochemical synthesis of metal alkoxides from the corresponding alcohols [11]. An electrochemical method allowed perfluoro- β -diketdiiminates of nickel, cobalt, copper and zinc to be obtained by the application of both electrodes made from the corresponding metals :



The chelates 2 are crystalline and volatile substances soluble in most organic solvents, such as ether, benzene, CCl_4 , C_6F_6 , CH_3CN . The characterization of these complexes is given in Table 1.

The NMR spectrum of the Ni complex has signals for trifluoromethyl groups (-10.4 p.p.m.; 6F; d; j = 16 c.p.s.) and vinylic fluorine atom ($+106$ p.p.m.; 1F; heptet) which correspond within 7 p.p.m. to their positions in the initial β -iminoamine. A vinylic fluorine atom is responsible for the splitting of trifluoromethyl groups into a doublet. All the protons on nitrogen appear as a broad unresolved band with the maximum at $\delta \sim 5.7$ p.p.m. Similar results are obtained for the Zn complex.

This data proves that these bis-bidentate complexes are strictly four-coordinated. An equivalence of all metal–nitrogen bonds is justified by the IR spectrum which exhibits symmetrical and antisymmetrical vibrations of ligand π -system within 1450 – 1600 cm^{-1} , and a strong absorption band within 3360 – 3390 cm^{-1} , corresponding to NH bonds.



The significant factor in the mass-spectra of complexes obtained is the tendency towards forma-

TABLE I. Characterization of Metal Perfluoro- β -diketdiiminates 2.

Metal	Melting point °C	Colour and crys- talline form	IR Spectrum (cm ⁻¹)		N.M.R. Spectrum in C ₆ F ₆ solution* 19F relative to CF ₃ COOH	Yields**		Analysis (calculated)				Molecular weight (mass-spectro- metrically)
			C = C/N	NH		I _H	%	C	H	N	M	
Co	169	brick-red needles	1448; 1586	3360	paramagnetic	2.1	53	24.00 (23.78)	1.19 (0.80)	11.13 (11.09)	11.60 (11.66)	505.118 (505.114)
Ni	184	green needles	1487; 1562	3382	-10.4 (6F, doublet) J = 16 cps. + 106 (1F, heptet)	1.9	42	23.54 (23.72)	1.13 (0.87)	11.05 (11.07)	11.52 (11.46)	504.883 (504.884)
Cu	163-164	red*** rhomb.	1480; 1565	3375	paramagnetic	2.2	40	24.03 (23.57)	1.11 (0.79)	10.73 (10.99)	12.50 (12.47)	509.712 (509.714)
Zn	183	pale-yellow rhomb.	1470; 1555	3390	-5.1 (6F, doublet) J = 18 c.p.s + 110 (1F, heptet)	2.3	47	24.15 (23.48)	1.16 (0.79)	11.01 (10.95)	12.45 (12.78)	511.557 (511.554)

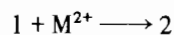
*19F shifts were measured relative to C₆F₆/lnt and then recalculated by the eqn. $\delta_{C_6F_6} = \delta_{CF_3COOH} + 88.0$. ¹H shifts were measured by δ scale relative to TMS/ext. **Percentage yields based on loss of electrode weight. ***Crystallohydrate of this complex is green; dehydration occurs at 120-130 °C.

tion of molecular ions, accompanied sometimes by metal valency change. The molecular ion of cobalt complex, for instance, is extremely stable, probably due to three valencies in the cobalt complex formation. As for the other complexes the initial radical cation (molecular ion) is formed as a result of electron removal from the ligand π -system. Additionally, double charged ions are observed. The main fragmentation proceeds with loss of a neutral ligand during first step (for Ni, Zn and Cu complexes) and loss of a second neutral ligand in the next one. In the case of Cu complex, where a lower valency of the central metal ion is possible, fragmentation occurs with loss of positive charged ligand, accompanied by copper ion reduction. Aside from these main fragmentation processes the departure of fluorine atoms and/or HF molecules and/or trifluoromethyl groups is observed. Further fragmentation of the ligand is similar to that of the initial iminoamine I.

The mechanism of electrochemical reaction is most likely similar to the electrochemical synthesis of metal alkoxides [11].

All the electrolyses were carried out by application of both electrodes made from the same metals. The initial anodic reaction comprised dissolution of anode material followed by formation of the corresponding metal tetrafluoroborates*. The formation of the metal perfluoro- β -diketdiiminates is a cathodic process. In order to estimate the reaction mechanism a special experiment has been carried out. In this case the cathode material was zinc and the anode lead; dissolution of Pb anode took place, along with lead deposition on the zinc electrode, followed by formation of zinc perfluoro- β -diketdiiminate. (Overmetalation of the cationic organolead compounds was described earlier [12].)

In order to justify the results obtained some attempts to synthesize metal perfluoro- β -diketdiiminates by a chemical exchange reaction have been made:



It was discovered that this reaction is going smoothly for copper acetate and nickel carbonate. All attempts to take into this reaction manganese, lead and cobalt acetates were unsuccessful. Copper and nickel chelates obtained by this chemical exchange reaction are equivalent to those obtained electrochemically.

Experimental

General

Melting points were taken on a Kofler melting point apparatus and are uncorrected. IR spectra were

*Tetrafluoroborate anion is derived from supporting electrolyte. The said metal tetrafluoroborates were isolated from the main products.

obtained in the solid state on a UR-20 spectrophotometer with pressed KBr disks. N.M.R. spectra were taken in C_6F_6 solution using a Perkin Elmer R-32 n.m.r. spectrometer. The fragmentation of the compounds was performed with an MS-30 mass-spectrometer.

Electrochemical Preparation of Metal Perfluoro- β -Diketdiimines-2

All the complexes were synthesized very similarly. A glass 15 ml cell without separation of anodic and cathodic spaces was applied. Two electrodes made from the corresponding metals with a surface area of 2–4 cm² were used. Electrolytes for all experiments comprised 2 ml (3.1 g) of initial perfluoro-iminoamine 1 as a reagent and 8 ml of 0.05 M acetonitrile solution of Bu_4NBF_4 as supporting electrolyte. The complex formations were performed by giving a long electrolysis (about 50 hr) at ambient temperature, at a current of 10–5 mA and a constant voltage of 6.64 V. After the end of the electrochemical reactions the electrolytes were evaporated to dryness *in vacuo*. The residues obtained were extracted several times with boiling hexane. After cooling the hexane extracts, the corresponding complexes were crystallized. An additional purification of the obtained complexes (especially for analytical purposes) was performed either by recrystallization from hexane or by sublimation at 130–140°/1 mm.

Chemical Preparation of Metal Perfluoro- β -Diketdiimines 2

The starting iminoamine 1 was refluxed for 1 hour with the Cu, Pb, Mn, Co acetates and Ni carbonate in benzene solution. After the end of the treatment the solutions were taken to dryness *in vacuo*. Then the isolation procedures above were repeated. After this it was discovered that only Cu and Ni complexes could be obtained by the above reaction conditions. It is necessary to mention that for the

Cu complex only a green crystallohydrate of 2 was obtained, but its sublimation yielded the red dehydrated complex. Equivalence of the Cu and Ni complexes obtained by chemical reaction with those obtained electrochemically was proved by superimposition of their IR spectra.

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