Inorganica Chimica Acta, 101 (1985) 141–145

Synthesis of Jäger Complexes of Fe, Co, Pd and Pt

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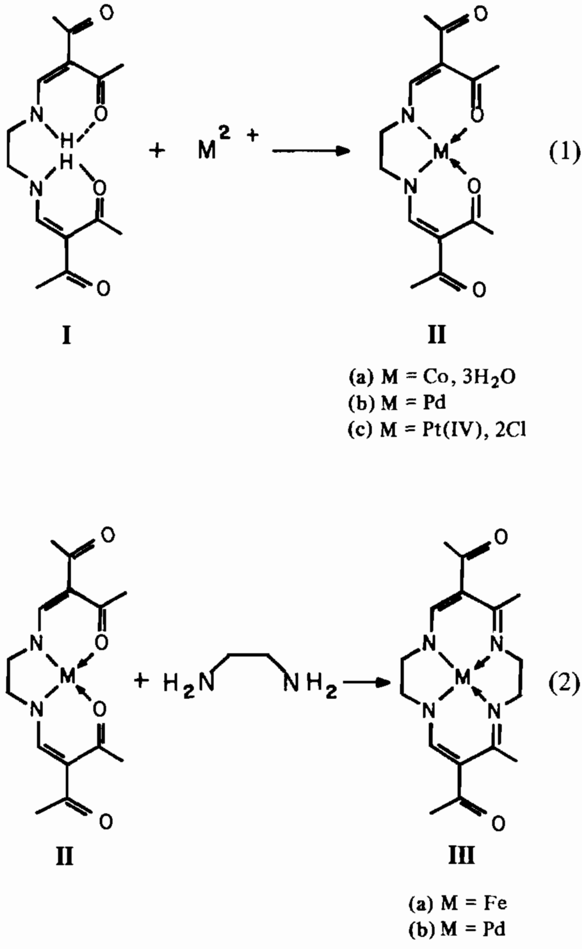
Received March 13, 1984

Abstract

The reaction 2,9-diacetyl-1,10-dimethyl-4,7-diazadeca-2,9-diene-1,10-dione with Fe(II), Co(II), Pd(II) and Pt(II) and the subsequent condensation of the formed complexes with ethylenediamine to give a macrocyclic complex are reported. The obtained products were characterized by elemental analysis, IR, electronic and NMR spectra. Pt(II) oxidates upon complexation giving a Pt(IV) complex. X-ray powder diffraction patterns indicate that the Pd uncyclic complex is isoestructural with its nickel analog.

Introduction

Much interest has been given to the synthesis of complexes containing tetradentate ligands, especially the macrocyclic ones, due to their properties [1] and to the possibility of relating them to biologically-important systems [2]. Among these complexes, those first synthesized by Jäger [3] have attracted attention due to their potential use as starting materials for synthetic protein models [4], to their redox properties [5] and to their behaviour as low dimension materials [6]. The preparation of these complexes is generally carried out via the formation of a complex from an open chain ligand, N_2O_2 coordinated, followed by a Schiff base condensation reaction to form the macrocyclic complex. For instance, nickel(II) and copper(II) undergo these reactions. Related complexes of other metals such as iron(II) and cobalt(II) have been prepared by different methods [7]. Some studies made with nickel and copper derivatives show the influence of the non-coordinated carbonyl group on the cyclization reaction [8], but no reports are available that show the influence of the metal ion. Here we report the results obtained with Fe(II), Co(II), Pd(II) and Pt(II). Scheme 1 shows the reactions and gives the identification for each compound.



I

II

(a) M = Co, $3H_2O$
(b) M = Pd
(c) M = Pt(IV), 2Cl

II

III

(a) M = Fe
(b) M = Pd

Scheme 1

Experimental

Preparation of Materials

All metal salts and organic materials were reagent grade products. All solvents were destilled prior to

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0020-1693/85/$3.30

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use. Metal complexes were prepared following the same procedure for nickel and copper complexes [9, 10].

Ligand **I** was prepared according to the literature procedure [9].

*2,9-Diacetyl-1,10-dimethyl-4,7-diazadeca-2,8-diene-1,10-dionecobalt(II)·3H_2O, **IIa***

To a boiling solution of one equivalent of ligand **I** in DMSO, a solution of one equivalent of the metal acetate in DMSO was added. The brown solution was stirred for 20 min and the solvent distilled off at reduced pressure. The powder was collected and recrystallized from ethanol. Yield 78%. *Anal.* Calcd. for $C_{14}H_{24}N_2O_7Co$: C, 42.42; H, 5.3; N, 7.07; Co, 14.89. Found: C, 42.35; H, 5.02; N, 6.92; Co, 15.3%. Mass spectrum, m/e calcd. for $C_{14}H_{18}N_2O_4Co$ = 337, m/e found = 337.

*2,9-Diacetyl-1,10-dimethyl-4,7-diazadeca-2,8-diene-1,10-dionepalladium(II), **IIb***

To a boiling solution of one equivalent of $PdCl_2$ in water, a slurry of one equivalent of the ligand in water was added. The solution was stirred until it turned light yellow (*ca.* 20 min). The solution was cooled and the crystals were collected by filtration of the mother liquor and washed with cold ethanol and water. The product was recrystallized from ethanol. Yield 87%. *Anal.* Calcd. for $C_{14}H_{18}N_2O_4Pd$: C, 43.75; H, 4.68; N, 7.29. Found: C, 43.53; H, 4.64, N, 7.24%. Mass spectrum, m/e calcd. = 384, m/e found = 384.

*Bischloro-2,9-diacetyl-1,10-dimethyl-4,7-diazadeca-2,8-diene-1,10-dioneplatinum(IV), **IIc***

To a warm solution of one equivalent of K_2PtCl_4 in water, a slurry of one equivalent of the ligand in water was added. The solution was stirred at room temperature for a period of approximately 8 weeks when a dark brown solid was formed. The product was collected by filtration and washed with cold water. The yield based on ligand **I** was 65%. *Anal.* Calcd. for $C_{14}H_{18}N_2O_4PtCl_2$: C, 30.88; H, 3.67; N, 5.14%. Found: C, 30.69; H, 3.27; N, 5.24%. Mass spectrum, m/e calcd. for $C_{14}H_{18}N_2O_4Pt$ = 473, m/e found = 473.

*6,13-Diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,12,14-tetraeneiron(II), **IIIa***

To a boiling solution of one equivalent of ligand in 1:1 ethanol–water, a solution of one equivalent of iron perchlorate in ethanol was added. The solution was stirred and a half-equivalent of NaOH in ethanol was added. The solution was stirred at its boiling point for 72 h. Then ten equivalents of ethylenediamine were added and the mixture heated for 24 h. The solution was cooled and a green powder collected and recrystallized from acetone–ethanol. Yield based on ligand **I**: 32.54%. *Anal.* Calcd. for $C_{16}H_{22}N_4O_2Fe$: C, 53.63; H, 6.14; N, 15.64. Found: C, 52.04; H, 7.60; N, 15.17%. Mass spectrum m/e calcd. = 358, m/e found = 358.

*6,13-Diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,12,14-tetraenepalladium(II), **IIIb***

One equivalent of complex **IIb** was dissolved in dry THF and heated to reflux under dry N_2 atmosphere. Ten-fold excess of ethylenediamine was added and the mixture heated for 20 min. The yellowish-green product was collected by filtration of the mother liquor and recrystallized from ethanol. Yield based on complex **IIb**: 87%. *Anal.* Calcd. $C_{16}N_{22}N_4O_2Pd$: C, 47.05; H, 5.39; N, 13.72. Found: C, 46.73; H, 5.26; N, 13.47%. Mass spectrum: m/e calcd. = 408, m/e found = 408.

Physical Measurements

Visible and ultraviolet spectra were obtained on a Perkin-Elmer 552 spectrophotometer with 1 cm quartz cells. Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 283 B spectrometer with KBr pellets and Nujol suspensions on CsI discs. ^1H NMR spectra were obtained on a Varian FT-80A spectrometer using tetramethylsilane as an internal standard. Thermogravimetric studies were carried out on a Perkin-Elmer TGS-2 thermogravimetric analyzer. Mass spectra were obtained using a Hewlett-Packard 5985B mass spectrometer. The electrical resistances of solutions of the soluble complexes were measured using a Beckman RC-20 conductivity bridge and a conductance cell with a cell constant of 0.1 cm^{-1}. Conductances were measured at 25 °C with approximately 10^{-3} M solutions. X-ray powder diffraction patterns were recorded on a Siemens D-500 Diffractometer with CuK_α radiation. Elemental analyses were performed by the Chemical Analytical Services of the University of California at Berkeley, Ca.

Results and Discussion

The reactions leading to complexes **II** and **III** of all metals were carried out in an analogous manner to that previously used for nickel and copper complexes [9, 10]. Simple modifications were made according to the nature of the metal. Solvent and temperature were the principal factors to be modified (see Experimental for details).

Palladium(II) underwent both reactions easily. It seems that palladium favors the template reaction, similarly to nickel and copper. Although platinum was expected to behave similarly to palladium, its complexation required much attention. Platinum(II) is oxidized during complexation to platinum(IV) and an hexacoordinated complex (**IIc**) with two Cl^-

TABLE I. Representative IR Bands for the Complexes (cm^{-1}).

I[a]	II Ni[a]	IIa	IIb	IIc	III Ni[a]	IIIa	IIIb	Assignment[b]
3418 mb[c]		3410 mb						O–H st
3200 m								O–H st
3000 w	3001 w	3000 w	2990 w	2990 w	2990 w			C–H st
	2925 w	2921 w	2920 w	2920 w	2950 w	2920 w	2905 w	C–H st
					2850 w	2840 w	2820 w	C–H st
1649 sh		1651 sh						O–H def
1640 m	1646 m	1640 m	1650 m	1645 m	1623 m	1610 m	1621 m	C=O
1630 m								C=O···H
	1590 vs	1588 vs	1592 vs	1593 vs				C=O···M
					1577 vs	1560 vs	1568 vs	C=N
1578 s	1573 s	1570 s	1575 s	1572 s	1558 s	1540 s	1555 s	C=C
					1499 s	1502 m	1500 m	
1450 m	1460 m	1460 m	1460 m	1455 m	1453 m			
1420 m	1412 s	1430 m	1435 w	1440 m	1436 m	1432 m	1430 m	methyl b
1400 s	1392 s	1391 s	1390 s	1390 s	1394 s	1380 s	1375 s	methyl b
1351 m	1364 m	1350 m	1358 s	1352 m	1340 s	1365 m	1360 s	methyl b
1240 m	1289 s	1280 s	1275 s	1270 s	1292 s	1280 s	1270 s	
1130 m	1112 m	1110 m	1100 m	1100 m	1090 m	1080 m	1100 m	
992 m	995 m	988 m	988 m	990 m				
930 m	942 m	935 m	935 m	932 m	935 m	930 m	935 m	
625 m	650 m	640 m	640 m	638 m	648 m	650 m	635 m	
552 m	535 m	520 w	515 m	525 m	548 m	580 w	610 w	
					500 m	520 m	510 m	
	412 m	450 m	400 m	420 m	400 w	420 m	398 m	M–N
				322 m				Pt–Cl

[a] See ref. [16]. [b] See ref. [14]. [c] Used abbreviations are: b, broad; m, medium, sh, shoulder; s, strong; vs, very strong; w, weak.

ligands is formed as is suggested by analytical and infra-red data [11] (Table I). However, this process takes a long time. Only occasional heating could be applied to accelerate the reaction as otherwise platinum was easily reduced to the metallic state. Progress of this reaction was followed by infrared spectroscopy as shown in Fig. 1, where the free ligand IR spectrum is compared with those of the products obtained at different stages. The IR spectrum of the final product shows the C=O band shifted to lower frequency with respect to the free ligand, but with a noticeable shoulder remaining at the same wavelength where the strong C=O band appears for the free ligand. This may be due to the fact that only two of the four C=O groups present in the ligand can be involved in the coordination, thus reducing the population of the corresponding absorption. All attempts made for the formation of the macrocyclic complex of platinum were unsuccessful because upon reaction with ethylenediamine complex **IIc** decomposed. The template reaction does not take place, probably due to the octahedral coordination of the metal, as the postulated mechanism for the ring closure reaction involves the take up of the axial positions by ethylenediamine [12].

The iron complex of the uncyclic ligand could not be isolated nor characterized and the condensation reaction to give complex **IIIa** had to be done *in situ*. The IR spectrum of the obtained green powder suggests that formation of the complex has proceeded. Its mass spectrum shows a peak with maximum r.a. and m/e equal to its calculated molecular weight, and it presents a fragmentation similar to those obtained for analogous complexes [13]. Due to its low solubility and high melting point, a pure sample of the product could not be obtained and its elemental analysis does not agree with the calculated value. Efforts are presently being made to obtain this complex in a pure form and to study its properties further.

Cobalt acetate reacts easily with ligand **I** to give the hydrated complex **IIa**. The presence of three water molecules in this complex is suggested by the loss of *ca.* 54 mass units at 110 °C determined by thermogravimetric analysis. This complex reacts further with ethylenediamine but the cyclization reaction does not proceed.

The most important bands in the infrared spectra of complexes **IIa**, **IIb**, **IIc**, **IIIa** and **IIIb** are shown in Table I and are assigned to vibrations of the ligand in accordance with published data [14]. The most important bands of the infrared spectra of the nickel complexes of systems **II** and **III** and of the free ligand **I** are also included for comparison. The main differ-

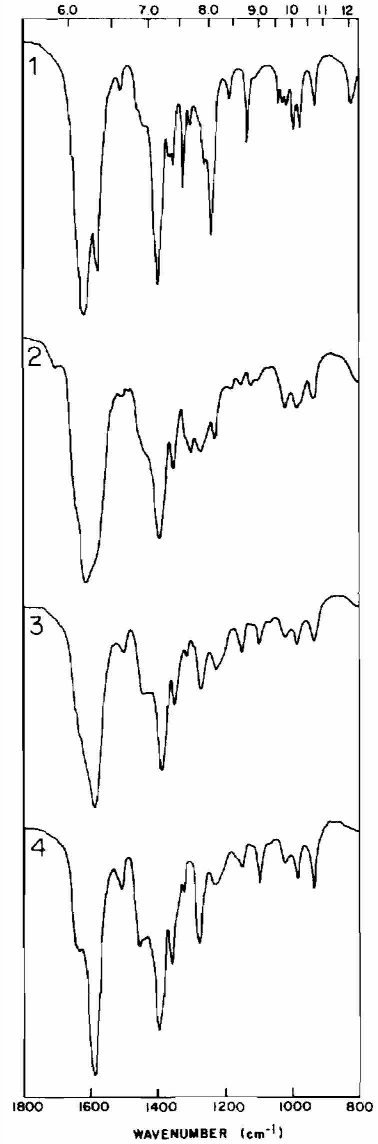

Fig. 1. Infrared spectra of the complexation of complex **IIc**: (1) Free ligand; (2–3) Intermediate steps; (4) Formed complex.

ences shown in Table I are those related to N–H, C=O and M–N vibrations, suggesting that coordination has been effected.

The electronic spectra of complexes **IIa**, **IIb** and **IIIb** were determined in the range 200–750 nm in ethanolic solutions. They are shown in Fig. 2. Due to the solubility of complexes **IIc** and **IIIa**, their absorption spectra could not be determined. The spectra of the palladium complexes **IIb** and **IIIb** present the characteristic absorption bands of palladium square planar complexes [15]. Measurements of the magnetic moments of these complexes show that they are diamagnetic, as expected.

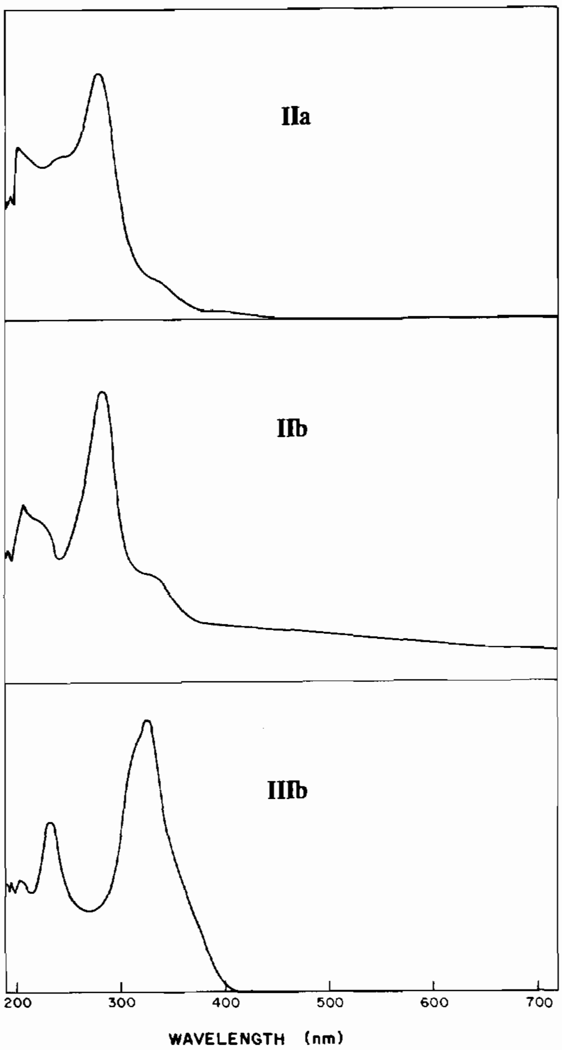

Fig. 2. Electronic spectra of the complexes in ethanol.

^{1}H NMR spectra of palladium complexes **IIb** and **IIIb** show the expected signals according to the proposed structure, in agreement with the spectra of the already reported nickel complexes [16]. The spectrum of complex **IIb** presents two signals for the methyl groups at $\delta = 2.35$ and $\delta = 2.60$, one peak corresponding to the methylene protons at $\delta = 3.65$ and one more for the vinyl proton at $\delta = 7.75$. Integration of the signals are 3:3:2:1 respectively. The ^{1}H NMR spectrum of complex **IIIb** shows equivalent peaks at the values of $\delta = 2.35$, 2.40, 3.7 and 7.9 with the corresponding integrations values 3:3:4:1, respectively.

The platinum complex **IIc** presents a ^{1}H NMR spectrum with four signals at $\delta = 2.32$, 2.45, 3.6 and 8.1 with integration 3:3:2:1. Satellite signals due to coupling with ^{195}Pt (34% abundance, $I = ½$) are present in the signals due to the vinyl and methylene

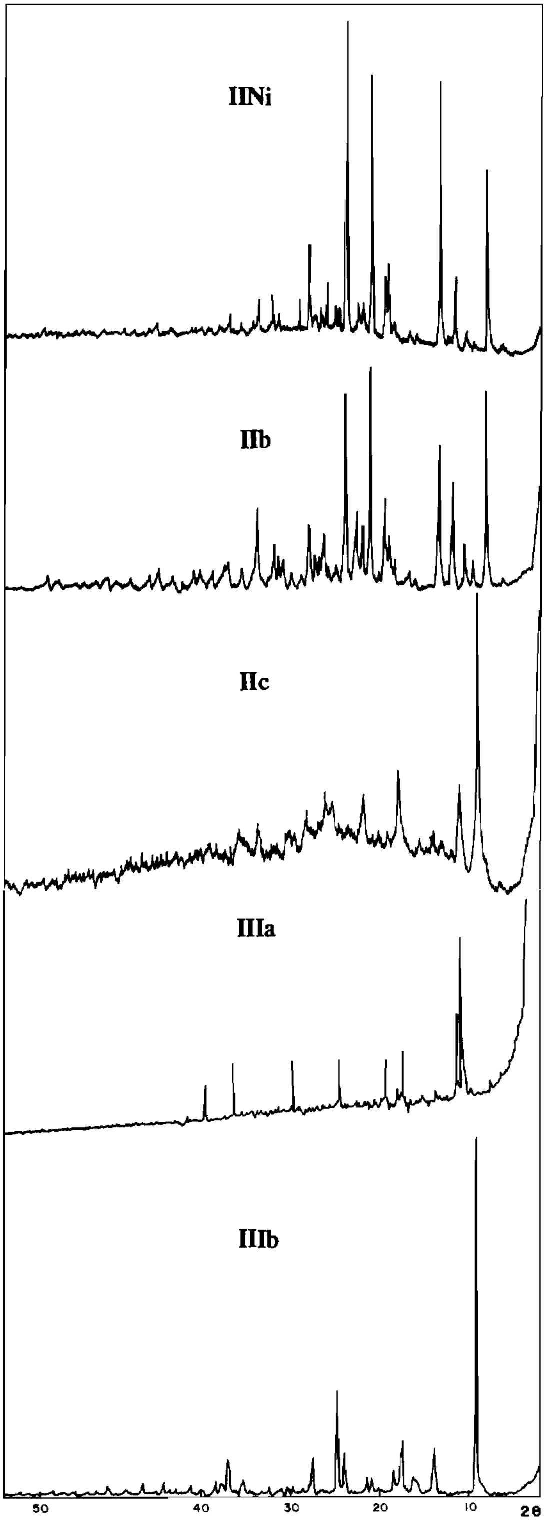

Fig. 3. X-ray powder diffraction patterns for the complexes.

protons with $J_{Pt-N-C-H}$ values of 20 Hz and 32 Hz, respectively.

The low conductivity values obtained for solutions of compounds **IIa**, **IIb** and **IIIb** indicated that the complexes are neutral as expected.

Figure 3 shows the X-ray powder diffraction patterns for the obtained complexes. For comparison, the pattern of the nickel uncyclic complex is included. From the patterns it is evident that the Pd and Ni uncyclic complexes are isomorphous. The Co uncyclic derivative does not show a powder diffraction pattern.

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