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Complexes of 2-furaldehyde 4-phenyl semicarbazone

Ghassan Ibrahim

Université Libanaise, Faculté des sciences, Beyrouth – Elhadath, Section I, Lebanon

Mustayeen A. Khan and Gilles M. Bouet*

Université d'Angers, Chimie de Coordination, Faculté de Pharmacie, 16 Boulevard Daviers,
F-49045 Angers Cedex 01, France

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Abstract

The synthesis of Co^{II} , Ni^{II} , Cu^{II} and Cd^{II} complexes of 2-furfural 4-phenyl semicarbazone (FPSC) with stoichiometric formulae: $[\text{M}(\text{FPSC})_2\text{X}_2]$ ($\text{M} = \text{Co}$, Ni or Cu ; $\text{X} = \text{Cl}$ or Br), $[\text{CuCl}_2(\text{FPSC})]$ and $[(\text{CdCl}_2)_2(\text{FPSC})]$ has been obtained for the first time. The complexes were characterized by elemental analysis, molar conductivity, magnetic measurements, i.r., far i.r. and electronic spectra. FPSC is deduced to act as a bidentate ligand in the Co^{II} , Ni^{II} and Cu^{II} complexes and as a tetradentate one in $[(\text{CdCl}_2)_2(\text{FPSC})]$.

Introduction

We have previously reported the synthesis and characterization of complexes obtained from 3-(2-furyl) 2-propenal semicarbazone (FASC) [1], 2-furaldehyde semicarbazone (FSC) and 5-methyl-(2-furaldehyde) semicarbazone (MFSC) [2]. The co-ordinating properties of various semicarbazones have also been studied [3–5] as well as those of many thiosemicarbazones [6–14]. In this paper, we present the synthesis and characterization of new metal complexes of 2-furfural 4-phenyl semicarbazone FPSC (Figure 1) and cobalt(II), nickel(II), copper(II) and cadmium(II) chlorides and bromides.

Experimental

Physical measurements

Physical methods have been described previously [1]. D.s.c. diagrams were recorded with a Mettler DSC 30 unit with the help of Mettler Toledo STAR^e System software (Unité de vectorisation particulière, UPRES-EA 2169, Faculté de Pharmacie, Angers, Pr. J. P. Benoit).

Fig. 1. Structural formula of FPSC.

The temperature range was 25–350 °C with a 10° per minute heating rate. Closed Al crucibles were used (40 μl) and the reference was an identical empty crucible.

Ligand synthesis

The 4-phenyl semicarbazide was dissolved in boiling distilled H_2O and an equimolar amount of freshly distilled furfural was added. The semicarbazone precipitated on cooling and was filtered off and recrystallized from boiling H_2O . The product had satisfactory mass and ^1H - and ^{13}C -n.m.r. spectra and melting point: 181 °C (lit. 185 °C [15]).

Dichlorobis(2-furfural 4-phenyl semicarbazone)-cobalt(II) (1)

A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.62 g, 0.011 mol) in EtOH 20 cm^3 was added to a solution of FPSC (2.29 g, 0.01 mol) in EtOH (40 cm^3) and reflux conditions were maintained for a total of 10 h. The solution became blue and the complex precipitated on cooling. It was filtered off, washed with small quantities of EtOH and *n*-pentane, dried and stored under reduced pressure at room temperature.

Dibromobis(2-furfural 4-phenyl semicarbazone)-cobalt(II) (2)

A solution of FPSC (2.27 g, 0.01 mol) in EtOH (45 cm^3) was heated to reflux and a solution of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ (3.42 g, 0.0055 mol) in EtOH (35 cm^3) was added dropwise. The mixture was boiled under reflux for 6 h. After standing at room temperature, the solution was heated to reflux for 4 h and the EtOH was removed by

* Author for correspondence

distillation while *n*-BuOH (80 cm³) was added. After 3 h at 80 °C, the complex precipitated. It was washed with EtOH only.

Dichlorobis(2-furfural 4-phenyl semicarbazone)-nickel(II) (3)

To a solution of FPSC (2.27 g, 0.01 mol) in EtOH (45 cm³) was added a solution of NiCl₂·6H₂O (1.18 g, 0.005 mol) in EtOH (16 cm³). After 4 h refluxing, the complex precipitated on cooling.

Dibromobis(2-furfural 4-phenyl semicarbazone)-nickel(II) (4)

A solution of NiBr₂ (1.20 g, 0.0055 mol) in *n*-BuOH (46 cm³) was added to a solution of FPSC in *n* BuOH (34 cm³). The mixture was heated to 90 °C for a total of 11 h. The complex precipitated on cooling.

Dichloro(2-furfural 4-phenyl semicarbazone)-copper(II) (5)

This complex was prepared by the method used for the complex (3) above.

Dibromobis(2-furfural 4-phenyl semicarbazone)-copper(II) (6)

A solution of CuBr₂·H₂O (3.32 g, 0.01 mol) in EtOH (40 cm³) was added to a solution of FPSC (2.27 g, 0.01 mol) in EtOH (40 cm³) at 80 °C. The mixture was boiled under reflux for 2 h. After 10 h at room temperature under constant stirring the complex had precipitated.

Tetrachloro(2-furfural 4-phenyl semicarbazone)-dicadmium(II) (7)

Equimolar amounts of CdCl₂ (1.82 g, 0.01 mol) and FPSC (2.36 g) each in EtOH (*ca.* 30 cm³) were mixed, and the solution heated to reflux. Complex (7) precipitated instantaneously.

Results and discussion

Analytical data

Analytical data for the new complexes are reported in Table 1. One series of [M(FPSC)X₂] complexes was obtained and, in addition, two other complexes of stoichiometries: [CuCl₂(FPSC)] and [(CdCl₂)₂(FPSC)]. The latter appears to be the first example of its type. According to their molar conductance values, these compounds are 1:1 electrolytes in solution, except for the cadmium(II) complex, which is a non-electrolyte.

I.r. spectra

The main i.r. bands are reported in Table 2. There is no indication of a band which could be assigned to the enol form of the compound [3, 16].

The bands assigned to the benzene ring remained quite unchanged when passing from the free ligand to the complexes. The breathing vibration of the furan heterocycle is shifted to lower wavelengths values in the case of [CuCl₂(FPSC)] and to higher values for [(CdCl₂)₂(FPSC)]. The breathing vibration band of the furan ring shows a significant shift, of 27 cm⁻¹, for the cadmium(II) complex only, indicating that the furan atom oxygen may be coordinated in this case. In all of the complexes, the carbonyl and C=N appear at lower wavenumbers compared to the free ligand.

The spectra of the complexes show some new bands compare to the free ligand, assigned to the metal-halogen and the metal-nitrogen bonds. The values reported in Table 2 agree with those previously described for these bonds [17]. Similarly, the ν(M—O keto) vibration band is observed in the range 350–390 cm⁻¹ for all the complexes. Finally, in the case of [(CdCl₂)₂(FPSC)], the ν(M—O furan) appears at 511 cm⁻¹ and this observation allows us to exclude a Cd—Cd bond [18, 19].

According to their i.r. spectra, the complexes may be therefore classified as follows. In [M(FPSC)₂X₂] (M = Co, X = Cl or Br; M = Ni, X = Cl or Br; M = Cu; X = Br), the ligand appears to be bidentate, coordinating through O (carbonyl) and N (imino) to give an octahedral geometry. In [CuCl₂(FPSC)], the

Table 1. Analytical data for the complexes

Compound	Colour	Yield (%)	M.p. ^a (°C)	Found (Calcd.) (%)			M	Λ ^b (S cm ² mol ⁻¹)	μ (B.M.)
				C	H	X			
(1) [CoCl ₂ (FPSC) ₂]	pink	66	201	49.1 (49.1)	3.7 (3.8)	12.3 (11.9)	9.2 (10.0)	21	4.8
(2) [CoBr ₂ (FPSC) ₂]	pink	35	259	42.3 (42.7)	3.4 (3.3)	23.2 (23.4)	7.6 (8.7)	40	3.8
(3) [NiCl ₂ (FPSC) ₂]	green	77	295d	49.3 (49.1)	3.9 (3.8)	12.1 (11.9)	10.0 (9.9)	40	3.1
(4) [NiBr ₂ (FPSC) ₂]	green	40	>300d	40.4 (42.7)	3.3 (3.3)	22.9 (23.4)	10.9 (8.6)	32	3.3
(5) [CuCl ₂ (FPSC)]	green	47	178d	39.7 (39.8)	3.1 (3.1)	19.5 (19.3)	17.2 (17.4)	24	2.1
(6) [CuBr ₂ (FPSC) ₂]	brown-green	56	172d	42.1 (41.3)	3.2 (3.2)	23.8 (23.5)	10.3 (9.3)	30	1.6
(7) [(CdCl ₂) ₂ (FPSC)]	white	77	>300d	24.3 (24.1)	1.8 (1.8)	23.8 (23.4)	37.0 (38.2)	7	diam.

^ad = dec.; ^bconductance of absolute EtOH: 10⁻⁸ S cm² mol⁻¹, conductance of NaI (10⁻³ mol dm⁻³ EtOH): 33 S cm² mol⁻¹.

Table 2. Main i.r. spectral vibrations for FPSC and its complexes

Compound	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	C-O-C	$\nu(\text{N-N})$	Furan breath.	Benz. ring	$\nu(\text{M-X})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$ ring	$\nu(\text{M-O})$ keto
FPSC	3354as 3194s	1686sh	1624	1285	935	1030	756 693	—	—	—	—
(1)	3264as 3142s	1657	1611	1277	932	1030	752 706	320	430	—	365
(2)	3258as 3194s	1647	1610	1275	930	1030	752 696	205	445	—	390
(3)	3264as 3142s	1680	1612	1277	932	1036	752 698	305	425	—	380
(4)	3254as 3192s	1651	1610	1277	930	1030	750 696	209	452	—	389
(5)	3283as 3161s	1669	1597	1275	930	1023	754 689	321	459	—	388
(6)	3204as 3148s	1665sh	1612	1281	928	1030	752 691	217	477	—	351
(7)	3298as 3212s	1659	1601	1271	936	1057	748 694	209	436	511	382

same coordinating atoms are probably involved, in a tetrahedral geometry. In the binuclear $[(\text{CdCl}_2)_2(\text{FPSC})]$ complex, FPSC presumably acts as a tetradentate ligand, coordinating through O (ring), N (imino), NH (imino) and O (carbonyl); the suggested structure of this complex is given in Figure 2.

Electronic spectra

The cobalt(II) chloro complex (1) shows three bands, ν_1 at 7870, ν_2 at 15,200 and ν_3 at 18,735 cm^{-1} . The bromo compound (2) also has three bands at 7765, 14,805 and 18,800 cm^{-1} . The ν_2/ν_1 ratios are 1.93 and 1.91 respectively, typical value for high spin octahedral cobalt(II) [20]. The calculated values of 10 Dq, according to König [21], are 7960 cm^{-1} (Cl) and 7710 cm^{-1} (Br) and the B (Racah parameter) values are 780 and 785 cm^{-1} respectively. These values are similar to those obtained for other high spin dihalogeno octahedral complexes [22].

Fig. 2. Proposed structure for $[(\text{CdCl}_2)_2(\text{FPSC})]$.

The nickel(II) complexes exhibit three bands at 7495, 13,020 and 25,000 cm^{-1} for complex (3) and at 7800, 13,410 and 24,240 cm^{-1} for complex (4). The first band ν_1 corresponds to the value of 10 Dq. The calculated values of B are 1015 cm^{-1} (Cl) and 930 cm^{-1} (Br) [21] and this is consistent with a distorted octahedral nickel(II) species with longer Ni-X bonds along the z axis, ionizing in solution (*cf.* Table 1).

The copper(II) complexes (6) and (7) present a broad band at *ca.* 12,200 cm^{-1} , quite symmetric and without any shoulder to allow us to determine 10 Dq. However, we may remark that the position of this band is closer to those of square-planar and/or tetrahedral species than those of octahedral complexes [22–24].

Thermal analysis

The main d.s.c. data are reported in Table 3. Free FPSC shows a fusion endotherm at 181 °C followed by a highly exothermic peak ($\Delta H = -128 \text{ kJ mol}^{-1}$) due to decomposition. Complex (1) shows a weak endothermic peak followed by an exothermic one, but these are too

Table 3. D.s.c. data for FPSC and its complexes

Compound	Temp. (°C)	ΔH (kJ mol ⁻¹)
FPSC	181 endo	+31.3
	239 exo	-128.4
(1)	251 endo	+2.6
	257 exo	-6.2
(3)	308 endo	+1.8
	312 exo	-1.4
(4)	164 endo	+13.6
	234 exo	+84.9
	303 exo	-91.3
(5)	188 endo	^a
	200 exo	-3.6
(6)	179 exo	-3.5
(7)	284 exo	-82.7
CdCl_2	185 endo	+18.6

^a Too weak to be calculated.

close together to allow an accurate calculation of the corresponding enthalpies. Complex (3) presents an endotherm at 308 °C, which is immediately followed by an exothermic peak at 312 °C. The bromide derivative (4) shows two large endotherms of low intensity at 164 and 234 °C respectively and an exothermic peak, corresponding to its decomposition, at 303 °C. The decomposition temperatures are identical for both nickel complexes and are related to that of the ligand. Under the same experimental conditions, the d.s.c. of the nickel(II) chloride hexahydrate exhibits three endotherms at 103, 193 and 244 °C respectively [25].

The copper chloro complex (6) begins to melt at 188 °C and then decomposes at 200 °C. Complex (7) does not show any endothermic peaks but only an exothermic decomposition peak at 179 °C.

The complex $[(\text{CdCl}_2)_2(\text{FPSC})]$ is very stable and only decomposes at 284 °C with the highest variation of enthalpy in the series: -83 kJ mol^{-1} . There are no other peaks before it. The d.s.c. diagram of cadmium chloride was also recorded under the same experimental conditions and only one endothermic peak at 185 °C was noted. The d.s.c. of a stoichiometric mixture of CdCl_2 and the ligand was also recorded. In this trace, two well defined endothermic peaks at 168 and 176 °C were observed along with some large endotherms around 200, 240 and 295 °C. This allows us to conclude that this complex $[(\text{CdCl}_2)_2(\text{FPSC})]$, with a higher thermal stability, is quite different from the other compounds in this series.

Conclusion

This new series metal complexes with 2-furfural 4-phenyl semicarbazone shows some differences with those previously described. Thus, it was possible to obtain a binuclear species from cadmium(II) chloride, $[(\text{CdCl}_2)_2(\text{FPSC})]$ which was not previously obtained. When a comparison is made with similar semicarbazones like 3-(2-furyl)2-propenal semicarbazone, 2-furaldehyde semicarbazone and 5-methyl-(2-furaldehyde) semicarbazone [1, 2], it is noted that the complexes deriving from FPSC involved the O (carbonyl) and the N (imine) atom as coordinating atoms and never coordinate through O (furan) and N (imine) or O (carbonyl) and O (furan).

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