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G Ibrahim, M A Khan, P Richomme, O Benali-Baitich, G Bouet. Synthesis and characterization of metallic complexes of 3-(2-furyl) 2-propenal semicarbazone with d element dihalides. Polyhedron, 1997, 16 (19), pp.3455-3461. 10.1016/S0277-5387(97)00063-6 . hal-03193520

HAL Id: hal-03193520

https://univ-angers.hal.science/hal-03193520v1

Submitted on 11 Apr 2021

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Pergamon

PII: S0277-5387(97)00063-6

Polyhedron Vol. 16, No. 19, pp. 3455–3461, 1997
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0277-5387/97 $17.00+0.00

Synthesis and characterization of metallic complexes of 3-(2-furyl) 2-propenal semicarbazone with *d* element dihalides

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(Received 28 June 1996; accepted 4 February 1997)

Abstract—3-(2-Furyl) 2-propenal semicarbazone (FASC) and Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} chlorides or bromides gave the complexes: $[M(FASC)_2X_2]$, $[M(FASC)_2]X_2$ or $[M(FASC)X_2]$ which were characterized starting from elemental analysis and molar conductances. Their structures are discussed on the basis of magnetic moments, infrared and electronic spectra; in addition, the NMR data are used in the case of Zn^{II} and Cd^{II} species. The main cell parameters are given using X-ray diffraction powder diagrams. © 1997 Elsevier Science Ltd

Keywords: complexes; *d* element; semicarbazone; spectroscopy; furan; X-ray powder diffraction.

We have previously described the complexes formed between various furan oximes and 3*d* metal dihalides [1]. The coordinating properties of some semicarbazones were studied [2–4] and many papers dealt with various thiosemicarbazone metal complexes [5–15]. As far as we know, no metallic complexes deriving from 3-(2-furyl) 2-propenal semicarbazone or FASC (see Fig. 1) have been described. In the present paper, we present nine new metal complexes obtained with FASC and Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} chlorides and bromides. The complexes were characterized using elemental analysis, infrared and electronic spectra and, in addition NMR spectra for diamagnetic species.

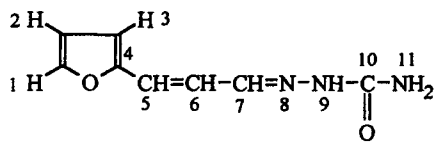

Fig. 1. Structure of FASC.

EXPERIMENTAL

Synthesis of the ligand [16]

To an aqueous solution (20 cm^3) of semicarbazide hydrochloride (11.15 g, 0.1 mol) and sodium acetate (20 g) was added dropwise an ethanolic solution (17.9 g in 20 cm^3) of β-furylacrolein (3-(2-furyl) 2-propenal). After three hours refluxing, the semicarbazone precipitated down on cooling. It was filtered and finally recrystallized from boiling water (yield 40%). The semicarbazone presented satisfactory analysis and spectral properties.

Synthesis of the complexes

All the complexes were prepared starting from 10^{-2} mol (1.79 g) of FASC dissolved in EtOH (used vol. in brackets). This solution was heated until the solvent

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refluxed and then, the ethanolic solution of the metallic halide was added slowly while stirring. The complexes were removed by filtration, washed with EtOH and *n*-pentane, dried *in vacuo* over silica gel. The purity of the complexes was verified using thin layer chromatography.

Dichloro bis[3-(2-*furyl*) 2-*propenal semicarbazone*] *cobalt(II)*. To the FASC ethanolic solution (50 cm^3) and under refluxing conditions, was added $CoCl_2 \cdot 6 H_2O$ (1.2 g; 5.10^{-3} mol; 20 cm^3). The reflux is maintained for 4 h and the volume is reduced by 50% under reduced pressure.

Dibromo bis[3-(2-*furyl*)2-*propenal semicarbazone*] *cobalt(II)*. The bromo complex was obtained in the same way as the chloro complex starting from FASC (70 cm^3) and $CoBr_2 \cdot 6 H_2O$ (1.6 g; 5.10^{-3} mol; 20 cm^3).

Dichloro bis[3(2-*furyl*)2-*propenal semicarbazone*] *nickel(II)*. It was prepared with FASC (40 cm^3) and $NiCl_2 \cdot 6 H_2O$ (1.2 g; 5.10^{-3} mol; 6 cm^3) after a 3 h reflux.

Dibromo bis[3-(2-*furyl*)2-*propenal semicarbazone*] *nickel(II)*. To the solution of FASC (70 cm^3) was added the solution of anhydrous $NiBr_2$ (1.1 g; 5.10^{-3} mol; 28 cm^3). The complex precipitated down on cooling after 4 h refluxing.

Dichloro bis[3-(2-*furyl*) 2-*propenal semicarbazone*] *copper(II)*. $CuCl_2 \cdot 2 H_2O$ (0.84 g; 5.10^{-3} mol; 25 cm^3) was added to FASC in EtOH (50 cm^3). The complex appeared instantaneously but the reflux was maintained for 2 h.

Dibromo bis[3-(2-*furyl*) 2-*propenal semicarbazone*] *copper(II)*. This bromo complex was obtained like the corresponding chlorocomplex using anhydrous $CuBr_2$ (1.12 g; 5.10^{-3} mol; 20 cm^3) and FASC (45 cm^3).

Dichloro [3-(2-*furyl*) 2-*propenal semicarbazone*] *zinc(II)*. To FASC (70 cm^3) was added the ethanolic solution of $ZnCl_2$ (1.36 g; 10^{-2} mol; 40 cm^3). The complex was obtained after 3 h refluxing and 50% reduction of the volume under reduced pressure.

Dichloro [3-(2-*furyl*) 2-*propenal semicarbazone*] *cadmium(II)*. Starting from FASC (70 cm^3) and $CdCl_2$ (1.8 g; 10^{-2} mol; 35 cm^3), the complex precipitated down during the addition of the metallic salt. However, the solution was refluxed for 1 h.

Dibromo [3-(2-*furyl*) 2-*propenal semicarbazone*] *cadmium(II)*. It was obtained in the same way as the chloro derivative with FASC (70 cm^3) and $CdBr_2 \cdot 4H_2O$ (3.4 g; 10^{-2} mol; 30 cm^3).

Physical measurements

Elemental analyses were carried out by the Service Central d'Analyse du C.N.R.S. (Vernaison, France). Melting points were determined with a Büchi Tottoli apparatus and were not corrected. Magnetic measurements were made at 298 K with a magnetic balance Bruker B-SU 10 (Laboratoire de Chimie de Coordination, U.S.T.H.B., Alger, Algeria) calibrating against $Hg[Co(SCN)_4]$ with correction of diamagnetism. Conductance values were obtained with a Tacussel CD6NG conductimeter at 298 K from 10^{-3} mol dm^{-3} solutions of complexes in absolute ethanol; the solvent had a conductance of 10^{-8} S cm^2 mol^{-2}; the conductance of NaI (10^{-3} mol dm^{-3}) was 33 S cm^2 mol^{-2}. The IR spectra were recorded with a Shimadzu FTIR-8010 M spectrophotometer between 4600 and 400 cm^{-1} (KBr disks) and with a Nicolet FTIR 20 F in the range 400–50 cm^{-1} using polyethylene disks (Laboratoire de Physique Cristalline, Institut des Matériaux de Nantes, France). Electronic spectra were recorded with a Perkin-Elmer Lambda 19 spectrophotometer from ethanolic or chloroformic solutions (10^{-3} mol dm^{-3}). The NMR spectra were obtained with a Jeol GSX 270 WB (270 MHz) spectrophotometer in D6-D.M.S.O. solutions, using TMS as internal reference. The X-ray powder diagrams were done with a Rigaku diffractometer (Laboratoire de Géologie, Faculté des Sciences, Université d'Angers) using the Cu-K_α radiation (1.5418 Å); the "Dicvol 91" [17] and "Celsiz" [32] computer programs allowed us to determine and refine the main crystalline parameters.

RESULTS AND DISCUSSION

Table 1 summarizes the analytical data of the complexes. Two series are obtained corresponding to the formula:

$[M(FASC)_2X_2]$ or $[M(FASC)_2]X_2]$ when M = Co, Ni or Cu;

$[M(FASC)X_2]$ when M = Zn or Cd.

The low molar conductances show that most of the complexes are non-ionic in ethanol. Moreover, the complexes obtained with $CoBr_2$ and $NiBr_2$ are ionic species in ethanol because their molar conductances are higher than that of NaI (Table 1).

Infrared spectra

The main vibration bands of the ligand and the complexes are reported in Table 2.

As the potential coordinating atoms are N(8), N(9), N(11), O (keto) and O (ring), we have to look at the main vibrations of the bonds including these atoms. The ligand exhibits a broad $N(11)H_2$ stretching vibration band at 3460 cm^{-1} (symmetric) and 3275 cm^{-1} (antisymmetric) while the ν(N(9)H) appears in the 3100–3250 cm^{-1} region. In addition, no band which might be due to ν(O—H) of an enolic form is observed above 3500 cm^{-1} [8,18]. This clearly establishes that FASC actually exists only in the keto form as indicated in Fig. 1. On the other hand, the ring vibrations, e.g. ring breathing or δ(C—O—C) are typical of 2-substituted furans [19].

In the spectra of the complexes several modifications occur. The ν(C=O) band is slightly shifted

Table 1. Analytical data

Compound	Colour	M.P. (°C)	Elemental analysis Found (Calc.) % C	H	M	X	μ (B.M.)	λ (S cm^2 mol^{-1})
$[CoCl_2(FASC)_2]$	green	252	39.1 (39.4)	3.7 (3.7)	12.0 (12.1)	14.2 (14.4)	4.90	26.1
$[CoBr_2(FASC)_2]$	green	264	33.5 (33.4)	3.3 (3.2)	10.1 (10.2)	27.4 (27.4)	4.87	30.8
$[NiCl_2(FASC)_2]$	tan	>300	39.2 (39.5)	3.8 (3.7)	12.1 (11.9)	14.3 (14.4)	3.19	23.5
$[NiBr_2(FASC)_2]$	tan	>300	33.2 (33.4)	3.2 (3.3)	10.1 (10.0)	27.5 (27.4)	3.21	51.1
$[CuCl_2(FASC)_2]$	tan	184	39.1 (39.1)	3.8 (3.7)	12.7 (12.8)	14.2 (14.3)	1.96	10.2
$[CuBr_2(FASC)_2]$	brown	175	33.1 (33.2)	3.1 (3.1)	10.8 (10.9)	27.2 (27.3)	1.85	9.7
$[ZnCl_2(FASC)]$	brown	243	30.7 (30.7)	3.0 (2.9)	20.3 (20.4)	22.1 (22.3)	diam.	3.7
$[CdCl_2(FASC)]$	tan	272	26.5 (26.5)	2.6 (2.5)	30.0 (31.4)	18.7 (19.3)	diam.	5.0
$[CdBr_2(FASC)]$	tan	242	21.3 (21.3)	2.1 (2.0)	22.7 (25.3)	33.9 (35.0)	diam.	7.0

to lower wave numbers in Cd^{II}, Ni^{II} and Co^{II} complexes and highly shifted in the other complexes. The ring breathing vibration band is shifted to higher wave numbers in the former and remains quite unchanged in the latter.

The metal–halogen stretching vibrations are observed in the spectra of the complexes [20]. In addition, the Co^{II}, Ni^{II} and Cd^{II} complexes exhibit a typical ν(M—N) vibration band [21(a)]. The Cu^{II} and Zn^{II} species show a metal–oxygen vibration band around 360 cm^{-1} corresponding to a keto oxygen atom [21(b)]. On the opposite side, the stretching vibration band of the carbon–nitrogen double bond of the azomethine group is always slightly shifted.

Some dimeric structures have been characterized in the case of copper$^{(II)}$ complexes with, for instance, the semicarbazones derived from isatin benzoin and 2-hydroxynaphthaldehyde [12]. But, we note that there is neither metal–metal stretching vibration band nor bridging metal–halogen vibration band [21] in our spectra. This indicates that these compounds are mononuclear species.

We note that FASC acts as a bidentate ligand through the N from the azomethine moiety in all cases and the O furanic atom in the case of cobalt, nickel and cadmium complexes or the O keto atom in the case of copper and zinc complexes whatever the number of FASC to be bound to the cation.

Electronic spectra

The electronic spectrum of the ligand presents no absorption in the visible and near IR region. The magnetic momentum (Table 1) indicate that the complexes are high spin species.

The spectra of the cobalt complexes show three bands respectively at 7390, 16,070 and 18,530 cm^{-1} (Cl^-) and 7410, 15,960 and 17,920 cm^{-1} (Br^-). The use of König's relations [22] lead to relative values of 10 Dq : 8590 cm^{-1} (Cl^-) and 8510 cm^{-1} (Br^-) while the Racah's B parameters are equal to 815 cm^{-1} and 770 cm^{-1} respectively and the β ratio (β = B free gaseous ion/B complex) is 0.84 and 0.79. In addition, the ν_1/ν_2 ratios : 2.17 for Cl^- ; 2.15 for Br^-, are located in the correct range for the attribution of the 3 *d–d* transition bands. Overall, the calculated and experimental values of the three *d–d* bands are quite identical and these values agree with a *trans* dihalogeno octahedral structure of the complexes [23(a)].

For the nickel(II) complexes the 3 bands are observed at 8465, 13,340 and 22,785 cm^{-1} in the case of Cl^- and 7925, 13,525 and 22,190 cm^{-1} for Br^-. The first band is equal to 10 Dq. The calculated B values are respectively 737 cm^{-1} ($\beta = 0.71$) and 765 cm^{-1} ($\beta = 0.73$). On the other hand there is no significant difference between experimental and calculated values of ν_1, ν_2, and ν_3. These values are in good agreement with those of *trans* dihalogeno octahedral structures [23(b)].

Finally for the copper(II) derivatives, the broad *d–d* absorption bands are located respectively at 13200 cm^{-1} for the chloride and 12,600 cm^{-1} for the bromide compound. This position is typical of a distorted octahedral structure [23(c)]. Moreover, the 10 Dq for the chloride derivative was calculated at 7125 cm^{-1} using Billing's equation [24]. This however was not possible in the case of the bromide complex because of the absence of shoulder bands.

NMR spectra

The NMR spectra (^1H and ^{13}C) of the ligand FASC and the diamagnetic species $[ZnCl_2(FASC)]$, $[CdCl_2(FASC)]$ are reported in Table 3.

^1H and ^{13}C resonances were attributed using heteronuclear correlations in ^2J and ^3J determined from the H.M.B.C. spectra of the compounds are presented in Fig. 2. The H(5)—H(6) coupling constant is 16 Hz while its value is 8 Hz for H(6)—H(7). Consequently the geometry around the C(5) and C(6) double bond is a *trans* arrangement and the single bond character of C(6)—C(7) is confirmed [25]. These values remained unchanged in the case of both the complexes.

The ^1H spectra do not show significant differences

Table 2. Main IR spectral vibrations

Compound	νNH_2 (11)	νNH (9)	$\nu C{=}O$ (10)	$\nu C{=}N$ (7, 8)	$\nu C{=}C$ (5, 6]	δCOC	$\nu C{-}N$ (10–11)	$\nu N{-}N$ (8–9)	Ring breath.	$\nu M{-}X$	$\nu M{-}N$ (8)	$\nu M{-}O$ ring	$\nu M{-}O$ keto
FASC	3460a 3275s	3202 3152	1662	1630	1589	1259	1172	974	1010	—	—	—	—
$[CoCl_2(FASC)_2]$	3424 3320	3233 3177 3113	1655	1622	1591	1246	1180	974	1024	210	264	481	—
$[CoBr_2(FASC)_2]$	3420 3320	3227 3171 3111	1657	1618	1591	1244	1180	972	1024	156	266	476	—
$[NiCl_2(FASC)_2]$	3414 3316	3233 3175 3113	1655	1620	1593	1246	1182	974	1026	207	260	477	—
$[NiBr_2(FASC)_2]$	3414 3314	3231 3177 3111	1655	1618	1593	1246	—	974	1024	253	277	476	—
$[CuCl_2(FASC)_2]$	3447 3266	3219 3169	1647	1618	1599	1257	1180	976	1018	321	271	—	357
$[CuBr_2(FASC)_2]$	3453 3368 3262	3212 3158	1645	1618	1591	1256	1182	976	1012	250	275	—	356
$[ZnCl_2(FASC)]$	3462 3347	3219 3085	1645	1628	1601	1265	1180	980	1010	328 302	194	—	361
$[CdCl_2(FASC)]$	3435 3333	3233 3123	1657	1622	1593	1254	1082	974	1024	229	185	480	—
$[CdBr_2(FASC)]$	3420 3329	3235 3123	1657	1620	1593	1252	1174	972	1020	155	186	479	—

Table 3. NMR data of FASC and its diamagnetic complexes (s = singlet, d = doublet)

	Chemical shift ^{1}H (ppm) [Coupling constants (Hz)]							Chemical shift ^{13}C (ppm) [Relative intensity (%)]							
	H(1) s	H(2), (H(3) and H(6)	H(5) d	H(7) d	H(9) s	H(11) s		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(10)
FASC	7.69	6.64–6.53	6.75 [$J_{5\text{-}6}$ = 16]	7.62	6.34	10.22		143.8 [88]	112.3 [74]	110.8 [100]	151.9 [95]	123.6 [92]	123.4 [85]	141.2 [90]	156.5 [86]
[$ZnCl_2$(FASC)]	7.70	6.66–6.54	6.76 [$J_{5\text{-}6}$ = 16]	7.62	6.35	10.22		143.9 [68]	112.4 [86]	111.0 [61]	151.9 [100]	123.7 [54]	123.5 [55]	141.5 [18]	156.6 [24]
[$CdCl_2$(FASC)]	7.71	6.67–6.54	6.76 [$J_{5\text{-}6}$ = 16]	7.63	6.35	10.23		143.9 [65]	112.4 [63]	110.9 [53]	151.9 [100]	123.7 [28]	123.5 [66]	141.5 [15]	156.5 [68]

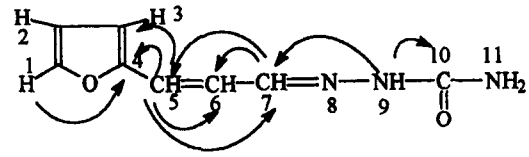

Fig. 2. ^{1}H/^{13}C couplings observed in the H.M.B.C. spectrum of FASC.

between the ligand and its complexes: neither chemical shifts nor coupling constants and multiplicity of the signals are perturbed by the chelation. This enhances the hypothesis that N(11) and N(9) are not coordinating atoms but the ligand is bonded with N(8) atom, as demonstrated on the basis of infrared spectra.

The chemical shifts observed in ^{13}C spectra (Table 3) of the complexes do not differ from those of FASC. These values are in good agreement with those given for similar compounds [2,26,27]. However, the relative intensities are modified: e.g. for C(10), the relative intensities are 86% in FASC against 24% and 68% respectively for [$ZnCl_2$(FASC)] and [$CdCl_2$(FASC)] (see Fig. 2). The keto O atom is therefore the coordinating atom in the case of [$ZnCl_2$(FASC)] only, and for the Cd^{II} compound the heterocyclic O is the second coordinating atom. Moreover, the C(5), C(6) and C(7) atoms are the more affected by this coordination. In addition, C(1), C(2) and C(3) relative intensities are shifted to lower values for the Cd^{II} complex than for the Zn^{II} compound.

These observations confirm (i) that the ligand shows a keto form and not an enolic one, and (ii) confirm our identification of coordinating atoms which was done on the basis of infrared spectra.

Powder diffraction

As very few compounds in these series of furanic complexes could give single crystals [28,29], we have chosen to carry out X-ray powder diffraction analysis.

The main parameters of the unit cell were determined with the "Dicvol 91" program [17]. The quantitative figure of merit F_N, where N is the number of lines used in the computation, should be as high as possible [30] since $F_N = 100$ means that the average discrepancy in 2θ calculation was $\leqslant 0.01°$. In our data, F_N lies from 17.5 to 7.7 meaning that the mean discrepancies in 2θ values lie in a range of 0.06–0.13°. This was obtained from the lines with highest intensities. The successive dichotomy method for indexing low symmetry lattices [31] indicates a triclinic system for the whole series.

The refined parameters using "Celsiz" [32] program are reported in Table 4. This table shows that the $CoBr_2$, $CuCl_2$, $CuBr_2$ complexes are likely to be isostructural. The two compounds [$CoCl_2(FASC)_2$] and [$CdBr_2$(FASC)] show higher values of the cell unit volume, the two cupric compounds exhibit almost the

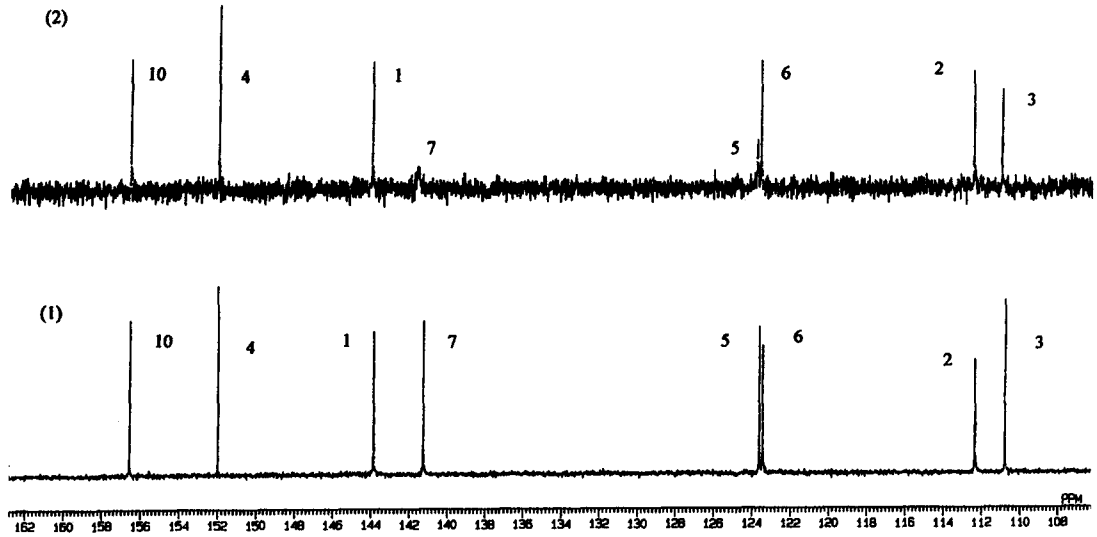

Fig. 3. ^{13}C NMR spectra of FASC (1) and $[CdCl_2(FASC)]$ (2).

Table 4. Refined cell parameters calculated from X-ray powder diagrams

Compound	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
$[CoCl_2(FASC)_2]$	11.960	12.053	12.935	108.27	96.44	108.91	1559.1
$[CoBr_2(FASC)_2]$	8.484	9.330	11.178	88.08	69.01	83.82	821.3
$[NiCl_2(FASC)_2]$	7.674	8.473	10.940	102.44	96.77	111.18	632.3
$[NiBr_2(FASC)_2]$	6.324	8.217	11.117	96.31	106.46	105.33	523.5
$[CuCl_2(FASC)_2]$	6.782	11.983	13.055	62.82	87.63	82.94	981.8
$[CuBr_2(FASC)_2]$	7.224	12.377	12.583	66.49	73.83	87.64	987.8
$[CdBr_2(FASC)]$	8.031	12.379	13.022	62.98	79.45	75.16	1111.4

same volume and the nickel(II) species present the smallest volumes. The highest volumes are correlated with higher values of α or β for $[CoCl_2(FASC)]$ and $CdBr_2(FASC)]$ or γ in the case of cupric complexes. In addition, the bromide complexes $[CoBr_2(FASC)_2]$ and $[NiBr_2(FASC)_2]$ exhibit smaller unit cells than analogous chloride species. In the mean time, these two compounds are the most ionic species in this series (see Table 1).

Compared with the case of single crystal analysis obtained with simple oximes (e.g. 2-furfuraldoxime) [29], the cell parameters remain in the same magnitude. In addition, though the relative intensities of the bands could obviously be different, the powder diagrams are closely similar to those observed with metallic complexes obtained with 2-furfuraldoxime and 2-thiophene aldoxime and FeX_2, NiX_2, (X = Cl or Br) [33]: the position of the main bands and their relative intensities are comparable.

CONCLUSIONS

We have synthesized and characterized seven new metallic complexes with 3-(2-furyl) 2-propenal semicarbazone (FASC) and *d* element halides. On the basis of analytical data, we have noted that they are non-ionic complexes and formulated as: $[M(FASC)_2X_2]$, $[M(FASC)_2]X_2$ and $[M(FASC)X_2]$. The spectral data indicated that they are mononuclear *trans* dihalogeno octahedral species and that FASC acts as a bidentate ligand through the N atom of the azomethine in all species and (i) the furanic O atom in the case of cobalt, nickel and cadmium complexes and (ii) the keto O atom for copper and zinc complexes. Indexations of the powder data led to triclinic solutions in every case.

Finally, some of these compounds such $[CuCl_2(FASC)_2]$ exhibit a cytotoxic activity and further experiments in this connexion have been undertaken and the results are to be published shortly [34].

Acknowledgements—The authors are indebted to Professor G. Moguedet and Dr R. Biagi (Université d'Angers) for their valuable technical assistance.

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