Pergamon

PII: S0277-5387(96)00606-7

Polyhedron Vol. 16, No. 15, pp. 2625-2629, 1997

0277-5387/97 $17.00+0.00

XPS study of aroylhydrazones containing triazole and their chelates

Ding-Bo Wang, Bao-Hua Chen, Bing Zhang and Yong-Xiang Ma*

Department of Chemistry, Lanzhou University, Lanzhou 730000, P.R. China

(Received 26 September 1996; accepted 6 December 1996)

Abstract—Three new aroylhydrazones including a triazole ring, 2-phenyl-1,2,3-triazolyl-4-carbaldehyde benzoylhydrazone (HL^1), 2-phenyl-1,2,3-triazolyl-4-carbaldehyde isonicotinylhydrazone (HL^2) and 2-phenyl-1,2,3-triazolyl-4-carbaldehyde salicyloylhydrazone (HL^3) and their chelates with some transition metal have been synthesized and studied using X-ray photoelectron spectroscopy (XPS). The XPS spectra show that the $2p$ electron binding energy (B.E.) of the metal ions (M_{2p}) and the $1s$ electron of the nitrogen atom coordinated are decreased and the $1s$ electron of coordinating oxygen atom is increased after coordination. During coordination, the direction of electron transfer is from the ligand to the metal ion ($L \rightarrow M$) and the coordination bonds formed are both of σ-type and π-type. © 1997 Elsevier Science Ltd

Keywords: aroylhydrazones; triazone ring; metal complexes; X-photoelectron spectroscopy.

Aroylhydrazones possess strong physiological activities and may inhibit many enzymatic reactions catalyzed by transition metals. They easily form chelate compounds with transition metals which also have stronger biological activities, so the coordination chemistry of aroylhydrazones and related compounds has been the subject of extensive studies [1–4]. But the studies of the charge transfer and the structure of these complexes by the XPS method have not been reported so far. In the present work, we report the synthesis of three new aroylhydrazone ligands containing the triazole ring and their chelates and have undertaken a systematic study using the XPS method for these compounds.

EXPERIMENTAL

Materials and measurements

Isoniazide, metal acetate and solvents were chemical reagent grade or analytical grade. 4-Formyl-2-phenyl-1,2,3-triazole was prepared as described in the literature [5].

The elemental analyses were carried out by a C. Erba elemental analyzer, model 1106. IR spectra were obtained with a Nicolet 170 SX spectrometer using KBr discs in the 200–4000 cm^{-1} region. UV spectra were determined with a Shimadzu UV-240 spectrometer in the range 200–700 nm using DMF solutions. XPS spectra were measured on a Escalab 210 spectrometer using a MgH K_α radiation ($h\gamma = 1253.6$ eV) at 10^{-8} Pa vacuum. The instrument power is 300 W (15 kV and 20 mA). The C_{1s} line (284.60 eV) in the sample was used as an internal standard. Thermal analyses were performed using a ME 800 FT miniature thermal analyzer from room temperature to 800°C in atmosphere.

Preparation of the ligands

1.73 g (10 mmol) of 2-phenyl-1,2,3-triazole-4-carbaldehyde in 80 cm^3 anhydrous ethanol were added dropwise into a solution of 1.36 g (10 mmol) of benzoylhydrazine in 80 cm^3 of anhydrous ethanol Then the mixture was acidified by several drops of acetic acid, heated for 3 h under reflux and cooled. The precipitate produced was separated by filtration, washed three times with hot ethanol and dried *in vacuo*. 2.7 g (93%) of white crystal products, HL^1 were obtained. HL^2 and HL^3 were obtained by the method similar to that of HL^1. The elemental analyses of these ligands are listed in Table 1.

---

*Author to whom correspondence should be addressed.

Preparation of chelates

The solution of the $M(OAc)_2 \cdot nH_2O$ (0.8 mmol) [M = Ni^{II}, Cu^{II} and Cd^{II}] in 10 cm^3 of anhydrous ethanol was added dropwise to 0.1 mmol of HL^1 (or HL^2, HL^3) in 5 cm^3 DMF under heating and stirring. The mixture was maintained under reflux for 2 h, then cooled, filtered, washed with ethanol and dried *in vacuo*. When preparing cobalt chelate, the $Co(OAc)_2$ must be dissolved in 10 cm^3 of 95% ethanol and a drop of glacial HOAc added to inhibit its hydrolysis.

RESULTS AND DISCUSSION

Composition and characterization

These ligands are all white crystalline solid, insoluble in general solvents such as ethanol, chloroform, acetone, benzene, carbon tetrachloride etc., but soluble in strong polar solvents, such as dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). Their chelates are only sparingly soluble in DMF and DMSO and are stable in the atmosphere. The yields and some properties of these ligands and their chelates are listed in Table 1 along with their elemental analyses, IR, UV, and thermal analyses.

The IR spectra of the ligands show the characteristic absorption bonds at 3153–3293, 1633–1669, 1544–1567, 1490–1503 and 966 cm^{-1} due to ν(N—H), ν(C=O), ν(N=C), ν(N—H), and ν(N—N), respectively. The IR spectra of the chelates reveal significant changes as compared to those of the ligands. The absorption band due to ν(N—H), ν(C=O) and ν(N—H) disappeared, but two new bands were observed at *ca* 1590 and 1272–1299 cm^{-1}, attributed to ν(C=N—N=C) and ν(N=C) band were shifted to lower frequency by *ca* 30–40cm^{-1} [6]. The characteristic band due to the phenyl ring of the ligands and their chelates is not changed.

These changes indicate clearly that the ligands undergo carbonyl enolization and then coordinate to metal ions through the azomethine nitrogen atom and the enolic oxygen atom.

The UV spectra of the chelates in DMF show that the *K* band (n-π^* transition) of the chelates suffers a bathochromic shift about 3.4–5 nm, l.c., the B band (n-π^* transition) is displaced by 40 nm as compared to those of their ligands.

The thermal analyses show that there are two endothermic peaks on the DTA curve of these ligands. The first appeared at 223, 212 and 292°C, respectively, which are the melting points of these ligands, because no loss of weight was observed on the corresponding TG curves. The second peak appeared above 350°C where the loss of weight on the corresponding TG curves indicated decomposition of the ligands. The decomposition is complete at about 600°C.

The thermal decomposition curves of the chelates are different from those of their ligands. There are no endothermic peaks, only a series of exothermic ones on the TDA curves, which shows there are no melting points for these chelates. They begin to decompose and are oxidized at *ca* 300°C and the residues correspond to the metal oxides. The TG curves of the $CoL^1_2 \cdot H_2O$, $NiL^2_2 \cdot H_2O$ and $CdL^2_2 \cdot H_2O$ show that their water molecules are lost at 192, 165 and 200°C, respectively, and their losses of weight are in agreement with the calculated values.

Table 1. Yields, properties and elemental analysis of the ligands and their complexes

Compound (formula)	Mol. wt.	Yield(%)	M.p.(°C)	Colour	Found (Calc.)(%) C	H	N
HL^1	291.3	93	222–223	White	66.1	4.5	23.9
($C_{16}H_{13}N_5O$)					(66.0)	(4,5)	(24.0)
HL^2	292.3	90	211–212	White	61.8	4.2	28.7
($C_{15}H_{12}N_6O$)					(61.6)	(4.1)	(28.8)
HL^3	307.3	92	291–292	White	62.5	4.3	22.8
($C_{16}H_{13}N_5O_2$)					(62.5)	(4.2)	(22.8)
$CoL^1_2 \cdot H_2O$	657.6	75	>300	Yellow	58.2	3.9	21.1
($C_{32}H_{26}N_{10}O_3Co$)					(58.4)	(4.0)	(21.3)
NiL^1_2	639.3	80	>300	Red	60.6	3.7	21.9
($C_{32}H_{24}N_{10}O_2Ni$)					(60.1)	(3.8)	(21.9)
CuL^1_2	644.2	68	>300	Brown	59.4	3.7	22.3
($C_{32}H_{24}N_{10}O_2Cu$)					(59.7)	(3.8)	(21.7)
$NiL^2_2 \cdot H_2O$	659.4	79	>300	Orange	54.3	3.6	25.2
($C_{30}H_{24}N_{12}O_3Ni$)					(54.6)	(3.7)	(25.5)
$CdL^2_2 \cdot H_2O$	713.0	72	>300	Yellow	50.6	3.4	23.5
($C_{30}H_{24}N_{12}O_3Cd$)					(50.5)	(3.4)	(23.6)
NiL^3_2	671.3	75	>300	Red	57.2	3.6	21.0
($C_{32}H_{24}N_{10}O_4Ni$)					(57.2)	(3.6)	(20.9)

XPS study of the ligands and their chelates

In recent years the XPS has been widely used in determing composition, electron structure and bonding features of some complexes in the solid state [7–11]. In the present work we discuss the charge distribution and charge transfer properties of coordinated nitrogen atom, oxygen atom and M^{2+} ions in aroylhydrazone chelates in the process of forming chemical bonds by the XPS determination. The XPS data of the ligands and their chelates are listed in Table 2. The XPS spectra of HL^1, HL^2, NiL^1_2 and NiL^2_2 are shown in Fig. 1.

It is can be seen from the XPS spectra that the composition data obtained by XPS for the ligands and their chelates agree with those of their elemental analyses. The spectra lines of the overlapping peaks for C, N and O atoms in the ligands and their chelates are peak fitted. Then it is found that the C_{1s} peak in ligands can be deconvoluted into three peaks, C^1_{1s}, C^2_{1s}, and C^3_{1s} which are the B.E. of C_{1s} due to —Ar, C=N— and C=O, respectively. The area ratio of the three peaks is in agreement with the ratio of three kinds of carbon atoms in the ligands. The N_{1s} peak can resolved into two peaks N^2_{1s} and N^3_{1s}, due to C=N and —N=. The area ratio of the peaks conforms with the ratio of two kinds of the nitrogen atom number in the ligands too. The binding energy of the amine N is greater than that of azomethine N, because the outer orbitals of the nitrogen atom in the azomethine are sp^2 hybridized, but those of the nitrogen atom in amine are non-equivalent hybridized orbitals. The electronegativity of the sp^2 hybridized orbitals is greater than that of sp^3 non-equivalent ones. Thus, the nitrogen atom in azomethine more easily attracts the electrons outside the nucleus of neighbouring atoms.

There is a N^1_{1s} peak (B.E. 399.0 eV) in the ligand HL^2, which can be due to the N_{1s} peak in the pyridyl ring, since the B.E. of the N_{1s} in pyridine is 398.8 eV [10].

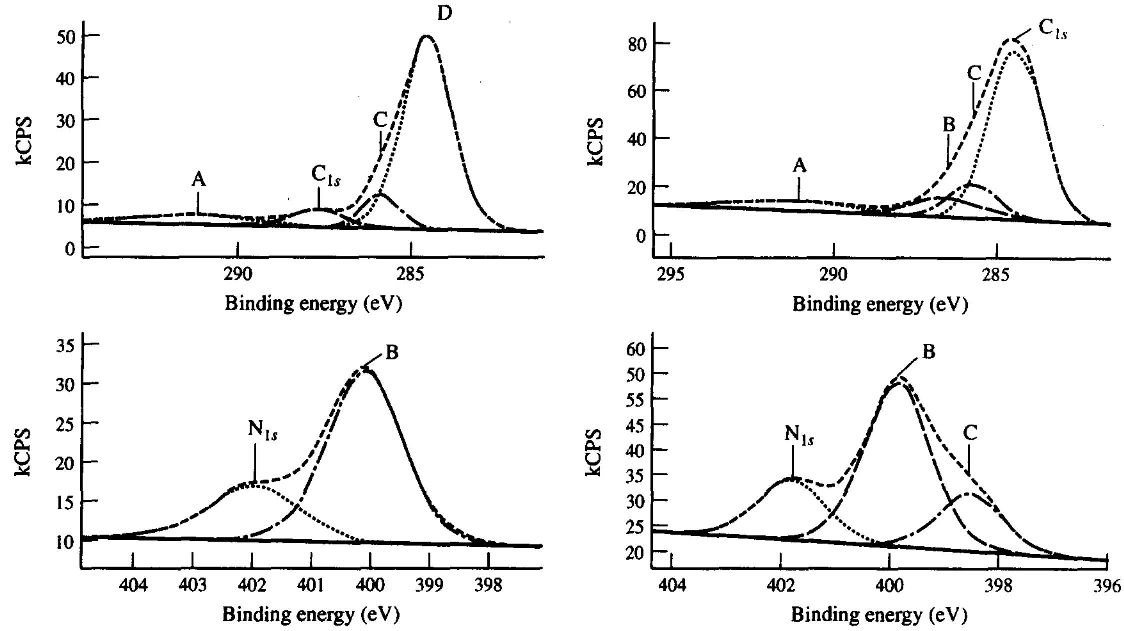
In addition to the ligand HL^3, only one type of oxygen exists in HL^1 and HL^2, so the O_{1s} peak is a singlet. But there are two O_{1s} peaks in the HL^3, namely O^1_{1s} and O^2_{1s} attributed to the oxygens in C=O and =OH [11], respectively, their area ratio is 1 : 1, which agrees with its composition.

The XPS spectra of the chelates show that the C^3_{1s} peak is shifted to lower binding energy, but O^1_{1s} to a higher one after forming chelates, which are due to loss of the H^+ after enolization of the carbonyl oxygen and forming a σ coordinate bond between O^- and M^{2+}. Because of the electron transfer of the oxygen to M^{2+}, the electron density outside the nucleus of the oxygen atom is decreased, but that of the carbon atom is increased. In addition, a new N^1_{1s} peak appeared in the chelates, but the B. E. of the N^1_{1s} is lower than that of N^2_{1s} in the azomethine since the nitrogen atom in the azomethine participates in coordination. The isolated electron pair of the nitrogen atom is donated to the empty orbitals of the central ion with forming a σ coordinate bond, while the empty antibonding π^* orbital of the nitrogen overlaps with the *d*-orbital of the central ion to form a π-bond, which is due to offering an electron only by the central ion, namely the backdonated π bond. The nitrogen in azomethine and the central ion form a σ—π coordinate bond, thus the electron density outside the nucleus of the azomethine nitrogen atom is increased relatively [8].

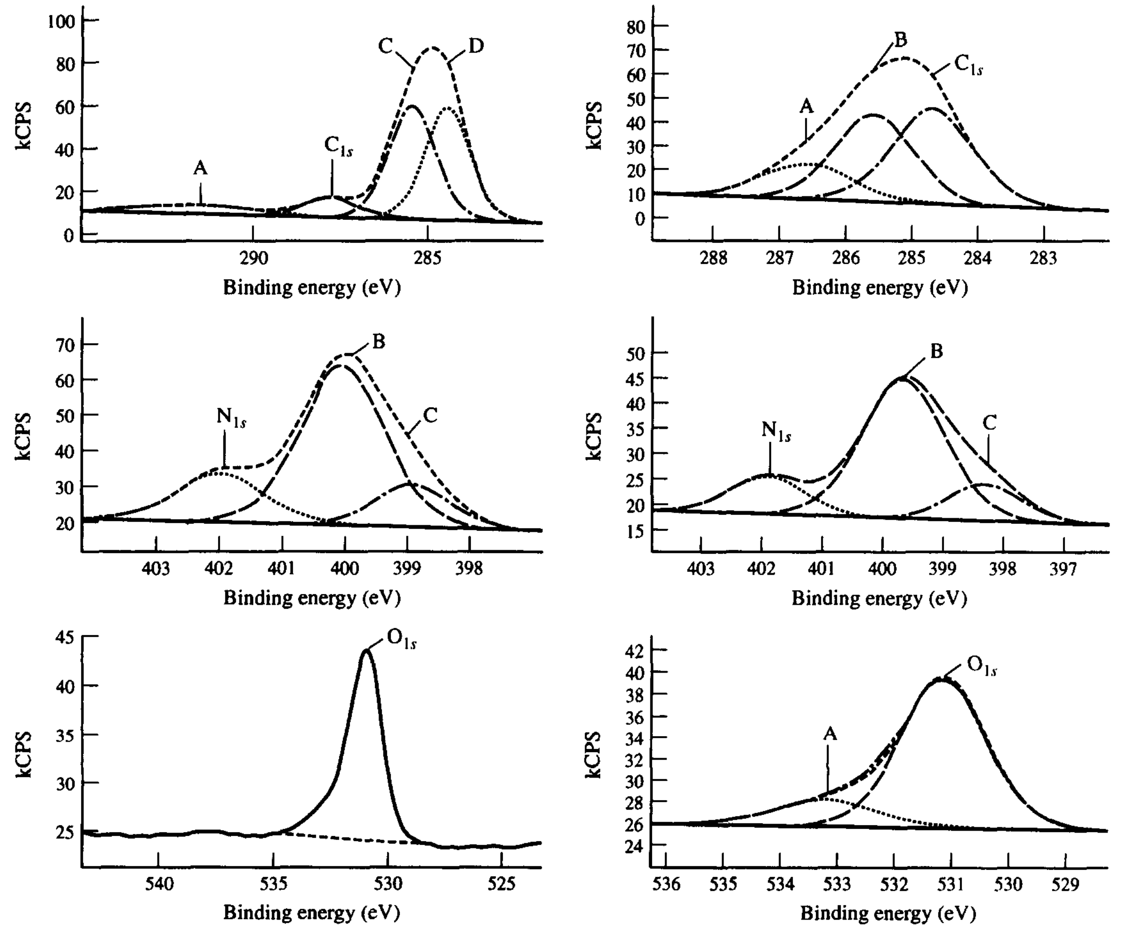
Table 2. XPS data of the metal salts, the ligands and their complexes

No	Binding energy (eV)[a]									
	C^1_{1s}	C^2_{1s}	C^3_{1s}	N^1_{1s}	N^2_{1s}	N^3_{1s}	O^1_{1s}	O^2_{1s}	$M^{3/2}_{2p}$	$M^{1/2}_{2p}$
$Co(OAc)_2 4H_2O$ [9]									782.55	798.10
$Ni(OAc)_2 4H_2O$ [10]									856.50	874.90
$Cu(OAc)_2$ [7]									935.00	955.00
$CdCl_2$ [7]									406.10	412.86
HL^1	284.6	285.9	287.7	—	399.8	402.0	530.9	—	—	—
$CoL^1_2 \cdot H_2O$	284.6	285.8	287.0	398.8	399.9	402.0	531.6	533.4	781.3	796.7
NiL^1_2	284.6	285.9	286.7	398.7	400.1	402.1	531.6	—	855.6	872.8
$CuL^1_2 \cdot H_2O$	284.6	285.8	286.7	398.5	399.9	402.1	531.4	533.1	934.7	957.4
HL^2	284.6	285.6	287.9	399.0[b]	400.1	402.0	530.4	—	—	—
$NiL^2_2 \cdot H_2O$	284.6	285.5	286.5	398.3	399.6	401.9	531.1	533.1	855.2	872.2
$CdL^2_2 \cdot H_2O$	284.6	285.4	286.5	398.3	399.5	401.8	531.1	533.5	404.9	401.6
HL^3	284.6	286.0	287.7	—	400.1	402.1	531.1	532.8	—	—
NiL^3_2	284.6	286.0	287.4	399.0	400.4	402.4	532.3	532.3	855.6	872.9

[a] C^1_{1s}, —Ar; C^2_{1s}, >C=N—; C^3_{1s}, >C=O; N^1_{1s}, $N=M^{2+}$; N^2_{1s}, >C=N—; N^3_{1s}, >N—; O^1_{1s}, >C=O; O^2_{1s}, —OH or H_2O.
[b] —C_5H_4N [10].



XPS spectrum (C_{1s} and N_{1s}) of complexs HL^1 and NiL_2^1



XPS spectrum (C_{1s}, N_{1s} and O_{1s}) of complexs HL^2 and NiL_2^2

Fig. 1. (a) XPS spectrum (C_{1s} and N_{1s}) of complexes HL^1 and NiL_2^1; (b) XPS spectrum (C_{1s}, N_{1s} and O_{1s}) of complexes HL^2 and NiL_2^2.

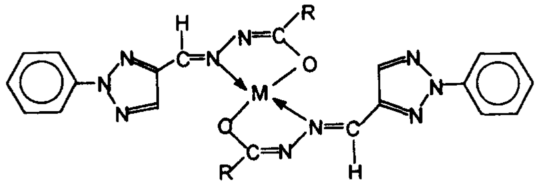


Fig. 2. Proposed structure for these chelates: M = Co, Ni, Cu and Cd. R = phenyl (HL^1), 4-pyridyl (HL^2) and o-hydroxyphenyl (HL^3).

The M $2p_{3/2}$ binding energy of the metal ion in the chelates is diminished as compared with that in acetate or chloride, because the metal ions not only donate electrons, but also accept them. Overall, the electron

The M $2p_{3/2}$ binding energy of the metal ion in the chelates is diminished as compared with that in acetate or chloride, because the metal ions not only donate electrons, but also accept them. Overall, the electron

density outside the nucleus is increased. While the binding energy of the N$^3_{1s}$ hardly changed before and after forming chelates, i.e. these nitrogen atoms do not participate in coordination to the central ions.

It is can be seen from the above discussion that the ligands are coordinated to the metal ions through the azomethine nitrogen atom and the enolized oxygen atom. Two coordinate bonds, a σ—π bond and a σ-bond, are formed between the azomethine nitrogen atom and the metal ion, and between the enolized oxygen and the metal ion, respectively. The direction of electron transfer is principally from the ligands to the metal ions.

Summarizing our results we propose a plausible structure for these chelates as shown in Fig. 2.

Acknowledgement—This work has been supported by the National Science Foundation of China.

REFERENCES

1. Patil, S. R., Kantak, U. N. and Sen, D. N., *Inorg. Chim. Acta* 1982, **63,** 261.
2. Biradar, N. S. and Havinale, B. R., *Inorg. Chim. Acta* 1976, **17,** 157.
3. Zhao, G. and Ma, Y. X., *J. Inorg. Chem.* 1989, **2,** 22.
4. Song, Q. B., Wu, X. L. and Ma, Y. X., *Polyhedron* 1994, **13,** 2395.
5. Mokhtar, H. and Soliman, R., *Carbohydrate Research* 1981, **90,** 144.
6. Lin-Vien, D., Colthup, N. B., Fateley, W. G. and Grasselli, J. G., *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules* 204. Academic Press, Inc., New York (1991).
7. Liu, S. H., Wang, D. H. and Pan, C. H., *X-photoelectron Spectrometric Analysis*. Science Press, Beijing (1988).
8. Haber, Vaclav and Ptacek, Pavel, *Inorg. Chim. Acta* 1991, **179,** 267.
9. Yang, G. W., Xia, X. P., Zhao, C. X. and Wang, D. F., *Chem. J. Chinese Universities* 1995, **16,** 55.
10. Nefedov, V. I., Zhumadilov, E. K. and Baer, L., *Zh. Neorg. khim.* 1978, **23,** 2113.
11. Burness, J. H., Sillard, J. G. and Taylor, L. T., *J. Am. Chem. Soc.* 1975, **97,** 6080.