

Synthesis and characterization of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with acetylacetonone *bis*-benzoylhydrazone and acetylacetonone *bis*-isonicotinoylhydrazone

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Summary

Acetylacetonone *bis*-benzoylhydrazone ($\text{PhCONHN}=\text{CMe}_2\text{-CH}_2(\text{LH}_2)$) and acetylacetonone *bis*-isonicotinoylhydrazone ($\text{NC}_5\text{H}_4\text{CONHN}=\text{CMe}_2\text{CH}_2(\text{L}'\text{H}_2)$) complexes of the types $[\text{ML}]$ and $[\text{ML}']$ ($\text{M} = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$ or Zn^{II}) have been prepared and characterized. All the complexes are non-electrolytes and the cobalt(II) complexes are low-spin, the nickel(II) complexes are diamagnetic and the copper(II) complexes are paramagnetic. The ligands chelate via two $\text{C}=\text{N}$ groups and two deprotonated enolate groups. The e.s.r. spectra of the copper(II) complexes indicate a tetragonally distorted dimeric structure. The X-ray diffraction parameters for $[\text{CoL}]$ and $[\text{NiL}']$ correspond to a tetragonal crystal lattice.

Introduction

Monoacylhydrazones of salicylaldehyde and many other similar ligands have been recognized as potential tridentate ligands where maintenance of π -conjugation markedly favours planarity⁽¹⁾. Metal complexes of such acylhydrazones, particularly the copper(II) complexes of 2-pyridine carboxylaldehyde-2'-pyridylhydrazone⁽²⁾ and salicylaldehyde benzoylhydrazone⁽³⁾ show antitumour activity. Similarly, metal complexes of 3- and 5-substituted salicylaldehyde *o*-hydroxybenzoylhydrazones⁽⁴⁾, salicylaldehyde benzenesulphonyl hydrazone⁽⁵⁾, furfurylidene and 5-nitrofurfurylidene benzoylhydrazones⁽⁵⁾ have been found to be bioactive. Besides these, transition metal complexes of isonicotinoylhydrazone have been found to be useful in polymer coatings, inks and pigments⁽⁶⁾.

Transition metal complexes of related ligands, viz. acetylacetonone *bis*-picolinoyl and *bis*-isonicotinoylhydrazones⁽⁷⁾, *bis*-2-furoylhydrazone⁽⁸⁾, glyoxal *bis*-benzoylhydrazone and salicylhydrazones⁽⁹⁾, diacetyl *bis*-benzoylhydrazone and benzil *bis*-benzoylhydrazone⁽¹⁰⁾ and diacetylpyridine *bis*-(4-methoxy benzoylhydrazone)⁽¹¹⁾ have been reported. In many cases the ligands have not been isolated but reactions between metal salts, acetylacetonone and the acylhydrazines have been carried out *in situ*. Acetylacetonone (2,4-pentanedione, $(\text{MeCO})_2\text{CH}_2$) has two active carbonyl groups, which may condense with two molecules of a monoacylhydrazone to give potentially multidentate ligands. We have prepared some bivalent transition metal complexes of the title ligands. The data are presented and discussed in this paper.

Experimental

Materials

All the chemicals were of BDH (AnalaR) or equivalent grade. Benzoylhydrazone (BH) was prepared by the

literature procedure⁽¹²⁾, whilst isonicotinoylhydrazone (INH) was obtained from CDH chemicals, New Delhi and recrystallized from EtOH.

Preparation of the Schiff bases

Acetylacetonone *bis*-benzoylhydrazone (LH_2) and acetylacetonone *bis*-isonicotinoylhydrazone ($\text{L}'\text{H}_2$) were prepared by reacting solid benzoylhydrazone (13.6 g) or isonicotinoylhydrazone (13.7 g) with acetylacetonone (5 cm^3) in 2:1 molar ratio under anhydrous conditions. The well-mixed reactants were heated on a water bath for ca. 1 h with occasional shaking. After ca. 10 min clear solutions were obtained. On cooling the reaction mixture and adding Et_2O the crude products were obtained, which were filtered off, dried in a desiccator over anhydrous CaCl_2 and recrystallized from hot EtOH. Acetylacetonone *bis*-benzoylhydrazone, m.p. 160°C (Found: C, 68.1; H, 6.1; N, 17.0. $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}_4$ calcd: C, 67.8; H, 5.9; N, 16.7 %.) Acetylacetonone *bis*-isonicotinoylhydrazone, m.p. 168°C (Found: C, 60.2; H, 5.2; N, 24.4. $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_6$ calcd: C, 60.3; H, 5.3; N, 24.8%.)

Preparation of the complexes

EtOH solutions of the metal(II) acetates (0.01 mol dm^{-3}) and Schiff bases (0.01 mol dm^{-3}) were reacted in a beaker. The complexes precipitated immediately. The reaction mixture was heated to 60°C for 5–10 min. The precipitates were filtered off by suction, washed several times with EtOH and dried in a desiccator over anhydrous CaCl_2 .

Characterization

Metal contents were determined by a literature procedure⁽¹³⁾, after digestion with aqua regia and evaporation of the residue with concentrated H_2SO_4 . C, H and N contents were determined microanalytically on a Perkin-Elmer 240 C model.

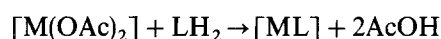
Molar conductances of $10^{-3} \text{ mol dm}^{-3}$ solutions in DMF/DMSO were measured at room temperature on a WTW conductivity meter. Room temperature magnetic susceptibilities of the complexes were determined with a Gouy type balance (Cahn, magnetic susceptibility apparatus) using $[\text{CoHg}(\text{SCN})_4]$ as calibrant and correcting the experimental magnetic susceptibilities for diamagnetism⁽¹⁴⁾.

Electronic and i.r. spectra of the Schiff bases and their complexes were recorded on Cary-2390 and Perkin-Elmer 783 spectrophotometers, respectively, in Nujol. X-band e.s.r. spectra were recorded on a Varian X-band spectrometer model E-4 at liquid N_2 temperature (LNT) in the solid state and DMF solution using tetracyanoethylene (TCNE) as g marker ($g = 2.00277$). Powder X-ray diffraction patterns were recorded on a Philips PW 1130 apparatus using CuK_α radiation. The physicochemical data are given in Tables 1–3.

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Results and discussion

Both LH₂ and L'H₂ may in principle exhibit keto–enol tautomerism involving the two RCONH groups, giving three possible tautomers. It appears from the analytical data of the complexes (Table 1) that the ligands are doubly deprotonated and give 1:1 (M:L) complexes in EtOH medium, in contrast to similar monodeprotonated or neutral ligands in aprotic solvents⁽¹¹⁾ or at low pH⁽¹⁰⁾. The ligands are doubly deprotonated in solvents of high dielectric constants on heating⁽¹¹⁾ or at high pH⁽¹⁰⁾. Since liberation of acetic acid in the reaction between the metal acetates and the ligands does not significantly affect the pH of the medium, the reaction may be written as



All the metal complexes are insoluble in common organic solvents such as ethanol, methanol, benzene, chloroform, acetone and ether, but are soluble in polar solvents such as DMF, DMSO and pyridine. The low molar conductance values of 10⁻³ mol dm⁻³ solutions of the complexes in DMF/DMSO at room temperature show that they are all non-electrolytes⁽¹⁵⁾.

Electronic spectra and magnetic moments

The electronic spectral data and μ_{eff} values are given in Table 1. [CuL] and [CuL'] show spectra similar to those

observed in several square planar complexes⁽¹⁶⁾. In contrast to the normal range of μ_{eff} values (1.8–2.2 BM) observed for copper(II) complexes, the slightly low values for [CuL] and [CuL'] suggest dimeric or polymeric structures.

The electronic spectra of the nickel(II) complexes suggest a square planar environment⁽¹⁷⁾, which is supported by their diamagnetism. Similarly, the spectra of the cobalt(II) complexes suggest a square planar geometry⁽¹⁸⁾. In contrast, the monodeprotonated and neutral ligands form 5- and 6-coordinated complexes, respectively, with copper(II) and nickel(II)⁽⁷⁾.

Infrared spectra

The i.r. spectra of the free Schiff bases (Table 2) show strong $\nu(\text{NH})$ bands between 3270 and 3200 cm⁻¹. The bands at 1660, 1570 and 1300 cm⁻¹ for LH₂ and at 1665, 1570 and 1330 cm⁻¹ for L'H₂ may be assigned to amide I, amide II and amide III, respectively⁽¹⁹⁾, suggesting that in the solid state the compounds exist primarily in the keto form. A strong band observed between 1630 and 1600 cm⁻¹ may be assigned to $\nu(\text{C}=\text{N})$ of the azomethine group⁽¹⁰⁾.

In the metal complexes, the absence of bands between 3400 and 3200 cm⁻¹ ($\nu(\text{NH})$) and at 1660 cm⁻¹ ($\nu(\text{C}=\text{O})$) and the appearance of a more intense band near 1600 cm⁻¹

Table 1. Analytical and electronic spectral data.

Complex	Colour	Decomposition Temperature (°C)	Found (Calcd.)(%)				μ_{eff} (BM)	Λ_m ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	λ_{max} (nm)
			M	C	H	N			
[CoL]	Reddish brown	> 300	15.0 (15.0)	58.2 (58.0)	4.8 (4.6)	14.3 (14.2)	2.1	32.8 ^a	1200, 445, 360 ² B _{2g} → ² E _g ; ² A _{1g} ; CT
[NiL]	Dark yellow	280	15.2 (15.0)	58.2 (58.0)	4.4 (4.6)	14.0 (14.2)	0.10	26.1 ^a	890, 540, 385 ¹ A _{1g} → ¹ B _{1g} ; ¹ B _{2g} ; CT
[CuL]	Green	234	15.6 (15.9)	57.3 (57.0)	4.4 (4.5)	14.3 (14.1)	1.66	10.1 ^a	595, 400 ² B _{1g} → ² A _{1g} ; ² E _g
[ZnL]	Light yellow	> 300	16.5 (16.3)	57.1 (57.1)	4.9 (4.5)	14.3 (14.0)	Diamagnetic	6.7 ^a	—
[CoL']	Dark brown	> 300	14.8 (14.9)	52.1 (51.6)	4.2 (4.0)	21.4 (21.2)	2.2	19.0 ^b	1210, 460, 277 ² B _{2g} → ² E _g ; ² A _{1g} ; CT
[NiL']	Red	> 300	15.0 (14.9)	52.4 (51.6)	4.3 (4.0)	20.8 (21.2)	0.15	25.0 ^b	825, 540, 350 ¹ A _{1g} → ¹ B _{1g} ; ¹ B _{2g} ; CT
[CuL']	Yellowish green	220	16.1 (15.9)	51.7 (51.1)	4.4 (4.0)	21.3 (21.0)	1.67	12.2 ^b	660, 400 ² B _{1g} → ² A _{1g} ; ² E _g
[ZnL']	Bright yellow	270	16.4 (16.2)	51.2 (50.9)	4.1 (4.0)	21.1 (20.9)	Diamagnetic	11.3 ^b	—

^aDMF; ^bDMSO.

Table 2. Important i.r. spectral bands and assignments.

Compound	$\nu(\text{NH})$	Amide I $\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{C}-\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
LH ₂	3270s	1660s	1630s	—	—	990s	—	—
L'H ₂	3200br	1665s	1630s	—	—	990s	—	—
[CoL]	—	—	1595m	1510s	1330w	1020s	440s	350w
[NiL]	—	—	1590s	1502s	1330w	1030s	400m	340w
[CuL]	—	—	1590s	1500s	1300w	1010w	450m	340w
[ZnL]	—	—	1600s	1510m	1330w	1020s	450w	350w
[CoL']	—	—	1610m	1500w	1340w	1020w	460m	360w
[NiL']	—	—	1610s	1500s	1350w	1010s	480m	350m
[CuL']	—	—	1610s	1495s	1340w	1025m	460s	350m
[ZnL']	—	—	1610s	1510m	1335w	1030s	480w	350w

Table 3. E.s.r. and bonding parameters for the complexes in DMF solution at 77 K.

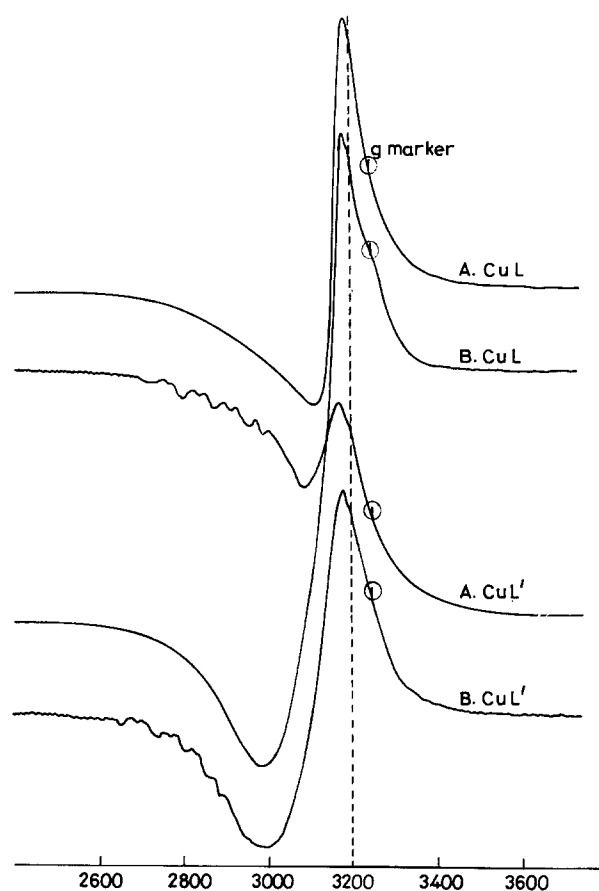
Complex	A_{\parallel} (G)	A_{\perp} (G)	A_{av} (G)	g_{\parallel}	g_{\perp}	g_{av}	g_{half}	α^2	β_1^2
[CuL]	106.67	63.33	77.77	2.2194	2.0417	2.1009	4.0771	0.55	0.69
[CuL']	93.33	83.33	88.66	2.2897	2.0482	2.1287	4.0864	0.58	0.67

due to $\nu(\text{C}=\text{N})$ compared to the free Schiff base indicate that both CONH groups are enolized and deprotonated⁽¹⁰⁾. Similarly, the amide II and $\nu(\text{C}=\text{N})$ bands of the ligands appear at a lower frequencies (ca. 20 cm^{-1}) in the complexes. The appearance of $\nu(\text{N}=\text{C}-\text{O})$ at ca. 1500 cm^{-1} and $\nu(\text{C}-\text{O})$ at ca. 1330 cm^{-1} in the metal complexes also suggest bonding to metal through both deprotonated C—O groups⁽²⁰⁾. $\nu(\text{N}-\text{N})$ is observed at higher frequency (ca. 20 cm^{-1}) than the free Schiff bases, confirming coordination of the azomethine nitrogen to the metal⁽²¹⁾.

Unperturbed ring vibrations at 990, 650 and 400 cm^{-1} in the free Schiff bases and their complexes suggest non-involvement of the phenyl or pyridyl ring in bonding. Weak bands at $480\text{--}440\text{ cm}^{-1}$ and $360\text{--}340\text{ cm}^{-1}$ are tentatively assigned to $\nu(\text{M}-\text{O})$ ⁽²²⁾ and $\nu(\text{M}-\text{N})$ ⁽²³⁾, respectively.

E.s.r. spectra

The solid state e.s.r. spectra of the copper(II) complexes exhibit an intense, broad signal with no hyperfine structure. The isotropic spectra give $A_{iso} = 26.67$ and 60.00 and

**Figure 1.** E.s.r. spectra of copper(II) complexes at 77 K: (A) In solid state; (B) in DMF solution.**Table 4.** Observed and calculated Q and hkl values.

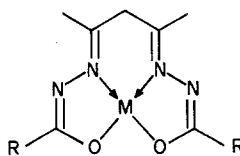
Powder pattern	2θ	Relative intensity	d	Q_{obs}	Q_{cal}	hkl
[CoL]						
1	7.120	216	12.4149	0.0065	0.0065	100
2	13.398	120	6.6085	0.0229	0.0229	001
3	16.037	128	5.5265	0.0327	0.0325	210
4	16.807	149	5.2750	0.0359	0.0359	111
5	21.524	187	4.1284	0.0586	0.0554	211
6	22.667	110	3.9228	0.0650	0.0650	310
7	24.380	155	3.6509	0.0750	0.0749	221
8	25.983	127	3.4291	0.0850	0.0845	320
[NiL']						
1	11.491	308	7.7072	0.0168	0.0168	100
2	12.063	333	7.3368	0.0185	0.0185	001
3	16.063	184	5.3339	0.0351	0.0353	101
4	20.195	338	4.3990	0.0517	0.0521	111
5	23.091	259	3.8517	0.0674	0.0672	200
6	24.448	154	3.6409	0.0754	0.0740	002
7	28.728	235	3.1073	0.1035	0.1025	211
8	32.603	174	2.7464	0.1326	0.1344	220

$g_{iso} = 2.0644$ and 2.1113 for [CuL] and [CuL'], respectively, suggesting the presence of grossly misaligned 'tetragonal' axes⁽²⁴⁾.

In frozen DMF solution, [CuL] and [CuL'] give axial spectra with two anisotropic pairs of g values (Table 3), suggesting a square planar stereochemistry with weak axial interaction of solvent molecules. The ordering of the g values, i.e. $g_{\parallel} > g_{\perp} > g_e$, indicates the presence of an unpaired electron in the $d_{x^2-y^2}$ orbital⁽²⁵⁾. All the four hyperfine lines observed in the g_{\parallel} region are further split into doublets, suggesting that the complexes are dimeric. This is supported by the presence of half-field signals in the spectra. The hyperfine splitting in the g_{\perp} region is not very clear (Figure 1).

A significant degree of covalent character in the metal–ligand bonds is indicated by the values of the σ -bonding parameter ($\alpha^2 = 0.50$ and 0.58) and π -bonding parameter ($\beta_1^2 = 0.69$ and 0.67), respectively⁽²⁶⁾.

On the basis of the above discussion, a general structure is proposed for the metal complexes (Scheme 1):

**Scheme 1**

where $M = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$ or Zn^{II} ; $R = \text{Ph}$ or NC_3H_4 .

X-ray diffraction studies

Since the complexes are very fine microcrystalline powders, comparatively few diffraction lines were obtained for [CoL] and [NiL'] compared to the crystalline benzoylhydrazine and isonicotinyhydrazine complexes⁽²⁷⁾ (Table 4). The observed patterns were indexed by Ito's method⁽²⁸⁾. The following lattice constants were obtained: [CoL], $a = b = 12.41$, $c = 6.60$ Å; [NiL'], $a = b = 7.70$, $c = 7.33$ Å. These values are consistent with a tetragonal crystal lattice.

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