

Six-Coordinate MN_4O_2 Bis-Chelates of A Brominated Pyridyl Semicarbazone: Electronic Structure, Optical Band Gap, Magnetic Behaviour, Nanocrystalline Microstructure and Antimicrobial Activity

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Abstract

The physical and biological properties of four neutral bis-chelates $[M(L^3)_2]$ ($M = Cu, Co, Ni, Zn$), formed by 6-bromopyridine-2-carbaldehyde semicarbazone (L^3H) acting as a monoanionic N,N,O-tridentate donor, are reported. Electronic absorption spectra in DMSO show intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands together with a ligand-to-metal charge-transfer band at 386-402 nm whose energy falls in the order $Zn > Ni > Co > Cu$, and weak Laporte-forbidden ligand-field bands ($\epsilon = 78-128 \text{ M}^{-1} \text{ cm}^{-1}$) for the three open-shell complexes. The d-d maxima lie at higher energy than those reported for semicarbazone chelates with MN_2O_2 or MN_2O_4 chromophores, as the substitution of two oxygen donors by two pyridine nitrogens requires. Direct-gap Tauc analysis gives $E_g = 3.69 \text{ eV}$ for the free ligand and 2.77-3.01 eV for the complexes, a narrowing of 0.68-0.92 eV that parallels the charge-transfer energies and places the compounds in the wide-band-gap semiconductor regime. X-band ESR spectra of the copper complex ($g_{\parallel} = 2.225$, $g_{\perp} = 2.189$) indicate a $d_{x^2-y^2}$ ground state in an environment of unusually small tetragonal anisotropy, while the observation of a well-defined anisotropic signal for the nickel complex, taken with $\mu_{eff} = 3.18 \text{ BM}$ from vibrating-sample magnetometry, excludes square-planar geometry outright and establishes a paramagnetic, six-coordinate d^8 centre. Room-temperature moments of 1.86 (Cu), 4.78 (Co), 3.18 (Ni) and 0.00 BM (Zn), with strictly linear M-H response and no hysteresis, confirm the +2 oxidation state throughout. All five solids are nanocrystalline and index on a monoclinic $P2_1/c$ cell, the ligand with $Z = 4$ and the complexes with $Z = 2$; Williamson-Hall analysis gives crystallite sizes of 30.8-45.4 nm and microstrain of 0.99-1.72 $\times 10^{-3}$. Thermogravimetry shows no mass loss below 232 $^{\circ}\text{C}$, excluding coordinated and lattice water, and resolves three stages terminating in the metal(II) oxide, whose mass matches calculation to within 0.18 % and so provides a gravimetric metal determination independent of EDAX. The nickel and cobalt complexes inhibit Gram-positive and Gram-negative bacteria, fungi and mycobacteria, the nickel complex reaching an activity index of 123 % against *Trichophyton rubrum* and the cobalt complex 111 % against *Mycobacterium bovis*.

Keywords: Pyridyl semicarbazone; Ligand-field spectra; Optical band gap; ESR spectroscopy; Magnetic susceptibility; Williamson-Hall analysis; Thermogravimetry; Antimicrobial activity

1. Introduction

Semicarbazones and their transition-metal complexes have been studied for more than half a century, both as structurally tractable models of how a flexible chelating chain adapts to a metal centre and as a source of antibacterial, antifungal, antitubercular and antitumour agents [1-5]. The donor set that a semicarbazone actually delivers is decided by the substituents on the parent carbonyl compound, because those substituents determine which proton is the most acidic and whether an auxiliary donor is present. A simple substituted benzaldehyde semicarbazone must enolise and binds as a uninegative N,O-bidentate chelate, saturating only four coordination positions; an o-hydroxy analogue loses the phenolic proton instead, retains a neutral carbonyl donor and becomes O,N,O-tridentate [6-8].

Replacing the carbocyclic ring by a pyridine ring bearing the azomethine group at the 2-position produces a third and distinct outcome. The ring nitrogen lies alpha to the carbon carrying the azomethine substituent and chelates alongside the azomethine nitrogen, but it carries no acidic hydrogen, so the hydrazinic N-H remains the only ionisable proton. The ligand therefore enolises, as a carbocyclic semicarbazone does, yet binds through three atoms rather than two, generating two fused five-membered chelate rings that share the azomethine nitrogen. In a companion study we established this binding mode for 6-bromopyridine-2-carbaldehyde semicarbazone (L^3H) and its copper(II), cobalt(II), nickel(II) and zinc(II) bis-chelates by elemental analysis, FT-IR, ^1H and ^{13}C NMR and

electrospray mass spectrometry, and formulated the complexes as neutral, anhydrous, non-electrolytic species $[M(L^3)_2]$ with a six-coordinate MN_4O_2 chromophore and the two tridentate ligands disposed meridionally [9].

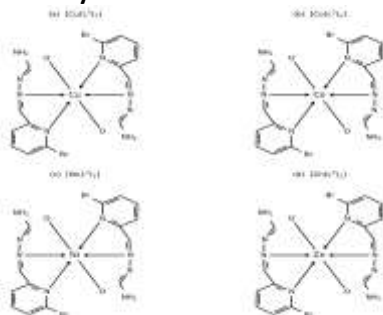
That formulation carries physical consequences which the connectivity evidence alone cannot test, and which are the subject of the present paper. Four of the six donors are now nitrogen. Since nitrogen lies above oxygen in the spectrochemical series, the ligand field should be appreciably stronger than in an MN_2O_2 or MN_2O_4 chromophore, and the d-d transitions should move to higher energy accordingly [10, 11]. The chelate architecture two rigid, planar, doubly fused tridentate arms wrapped about the metal should also enforce an environment closer to a regular octahedron than a flexible bidentate ligand can achieve, which is testable through the g-tensor anisotropy of the copper complex and through the orbital contribution to the magnetic moments. Most decisively, the nickel complex provides an unambiguous geometric test: a square-planar d^8 centre is diamagnetic and ESR-silent, whereas a six-coordinate one is not.

2. Experimental

2.1. Compounds

6-Bromopyridine-2-carbaldehyde semicarbazone (L^3H , $C_7H_7BrN_4O$, $M_r = 243.06 \text{ g mol}^{-1}$) was prepared by microwave-assisted, acetate-buffered condensation of 6-bromopyridine-2-carbaldehyde with semicarbazide hydrochloride in ethanol-water, and the complexes $[M(L^3)_2]$ ($C_{14}H_{12}Br_2MN_8O_2$; $M = Cu, Co, Ni, Zn$) by reaction of the ligand with the corresponding hydrated metal(II) acetate in a 2:1 ligand-to-metal molar ratio under intermittent microwave irradiation at 300-450 W. Full synthetic detail, elemental analyses, FT-IR, NMR and mass-spectrometric characterisation and the structural formulation are given elsewhere [9]. Composition, purity and the N,N,O-tridentate binding mode are taken as established in what follows, and the resulting structures are shown in Fig. 1.

Fig. 1. Structures of (a) $[Cu(L^3)_2]$, (b) $[Co(L^3)_2]$, (c) $[Ni(L^3)_2]$ and (d) $[Zn(L^3)_2]$, established in [9]. Each metal is chelated by two uninegative N,N,O-tridentate ligand anions binding through the pyridine nitrogen, the azomethine nitrogen and the enolate oxygen, giving a six-coordinate MN_4O_2 chromophore with the ligands disposed meridionally.



3. Results and discussion

3.1. Electronic absorption spectroscopy

The maxima, molar absorptivities and assignments are given in Table 1 and the spectra in Fig. 2. Molar absorptivities follow from the Beer-Lambert relation (Eq. 1), and the corresponding wavenumbers and transition energies from Eqs. 2 and 3.

$$A = \epsilon c l \quad \text{and hence} \quad \epsilon = A / (c l) \quad (1)$$

$$\tilde{\nu} (\text{cm}^{-1}) = 10^7 / \lambda (\text{nm}) \quad (2)$$

$$E (\text{eV}) = hc / \lambda = 1239.84 / \lambda (\text{nm}) \quad (3)$$

3.1.1. Intraligand transitions

The free ligand shows two bands. The intense absorption at 253 nm ($\epsilon = 21\,500 \text{ M}^{-1} \text{ cm}^{-1}$) is the $\pi \rightarrow \pi^*$ transition of the pyridine ring conjugated with the azomethine group, and that at 305 nm ($\epsilon = 11\,800 \text{ M}^{-1} \text{ cm}^{-1}$) is the $n \rightarrow \pi^*$ transition of the azomethine chromophore [10, 13]. Both persist in the complexes, the $\pi \rightarrow \pi^*$ band shifting slightly to 259-263 nm and the $n \rightarrow \pi^*$ band undergoing a systematic bathochromic displacement of 21-29 nm to 326-334

nm as coordination of the azomethine nitrogen lowers the energy of the C=N π^* orbital relative to the nitrogen lone pair. It is worth noting that L³H shows no third band of the kind observed near 395 nm for o-hydroxy semicarbazones, where an intramolecular charge transfer occurs across a hydrogen-bonded phenol [7, 8]. This ligand has no phenol, its absorption edge accordingly lies at much shorter wavelength (336 nm), and its optical band gap is correspondingly large, as Section 3.2 shows.

3.1.2. Charge-transfer bands

A new, moderately intense band appears in every complex between 386 and 402 nm ($\epsilon = 4\,800\text{--}6\,900\text{ M}^{-1}\text{ cm}^{-1}$) with no counterpart in the free-ligand spectrum. It is assigned to ligand-to-metal charge transfer from the filled orbitals of the enolate oxygen and the two nitrogen donors into the empty or partly filled d orbitals of the metal. Its energy decreases in the order Zn (386 nm) < Ni (392 nm) < Co (396 nm) < Cu (402 nm); that is, the transition falls in energy as the metal becomes a better electron acceptor. The ordering follows the effective nuclear charge and the Irving-Williams sequence [14] and reproduces the $\nu(\text{M-O})$ and $\nu(\text{M-N})$ frequency ordering established independently by vibrational spectroscopy [9].

3.1.3. Ligand-field transitions and the strength of the field

Weak, Laporte-forbidden d-d absorptions ($\epsilon = 78\text{--}128\text{ M}^{-1}\text{ cm}^{-1}$) are observed for the three open-shell complexes and are absent, as required, from the d¹⁰ zinc spectrum. [Cu(L³)₂] gives a single broad envelope centred at 615 nm (16 260 cm⁻¹). For a d⁹ ion the three components of the ²E_g → ²T_{2g} manifold are rarely resolved, and the position of the envelope is characteristic of a CuN₄O₂ chromophore [11, 15].

[Co(L³)₂] shows two bands, at 505 nm (19 802 cm⁻¹) and 630 nm (15 873 cm⁻¹), assigned to ν_3 , ⁴T_{1g}(F) → ⁴T_{1g}(P), and ν_2 , ⁴T_{1g}(F) → ⁴A_{2g}, of a high-spin octahedral d⁷ configuration; the lowest transition ν_1 , ⁴T_{1g}(F) → ⁴T_{2g}, lies in the near infrared beyond the range of the measurement [10]. The low molar absorptivities indicate a chromophore retaining an approximate centre of symmetry, which is itself an argument for octahedral rather than tetrahedral coordination, since tetrahedral cobalt(II) typically gives ligand-field bands one to two orders of magnitude more intense.

[Ni(L³)₂] shows two bands, at 440 nm (22 727 cm⁻¹) and 592 nm (16 892 cm⁻¹), assigned to ν_3 , ³A_{2g} → ³T_{1g}(P), and ν_2 , ³A_{2g} → ³T_{1g}(F), of an octahedral d⁸ centre. An octahedral rather than a square-planar assignment is adopted because it is the only interpretation compatible with the magnetic moment of 3.18 BM and the anisotropic ESR spectrum reported in Sections 3.3 and 3.4: a square-planar nickel(II) complex would be diamagnetic and ESR-silent, and this one is neither. It should be noted, however, that the 440 nm feature lies on the low-energy tail of the intense LMCT band, so that its maximum is subject to appreciable uncertainty; the ratio $\nu_3/\nu_2 = 1.35$ obtained from the two observed bands is lower than the 1.5–1.75 usual for octahedral nickel(II), and no attempt has therefore been made to extract Dq and the Racah parameter B by Tanabe-Sugano fitting. The lowest transition $\nu_1 = 10\text{ Dq}$ lies beyond the measured range, and its direct observation in the near infrared would be required for a reliable parameterisation.

The comparison that the donor set predicts is nevertheless borne out. Copper d-d envelopes for semicarbazone bis-chelates with MN₂O₂ and MN₂O₄ chromophores are typically reported near 640–655 nm, cobalt ν_3 near 520–530 nm and nickel ν_2 near 610–620 nm [6–8, 16]; the corresponding values here are 615, 505 and 592 nm. In every case the present complexes absorb at higher energy, that is, they experience the strongest ligand field. This is exactly what an MN₄O₂ chromophore requires: because nitrogen lies above oxygen in the spectrochemical series, replacing two oxygen donors by two pyridine nitrogens raises the ligand-field splitting and moves the d-d bands to shorter wavelength [10, 11]. The electronic spectra thus supply a quantitative confirmation of the donor set deduced from the vibrational and NMR evidence.

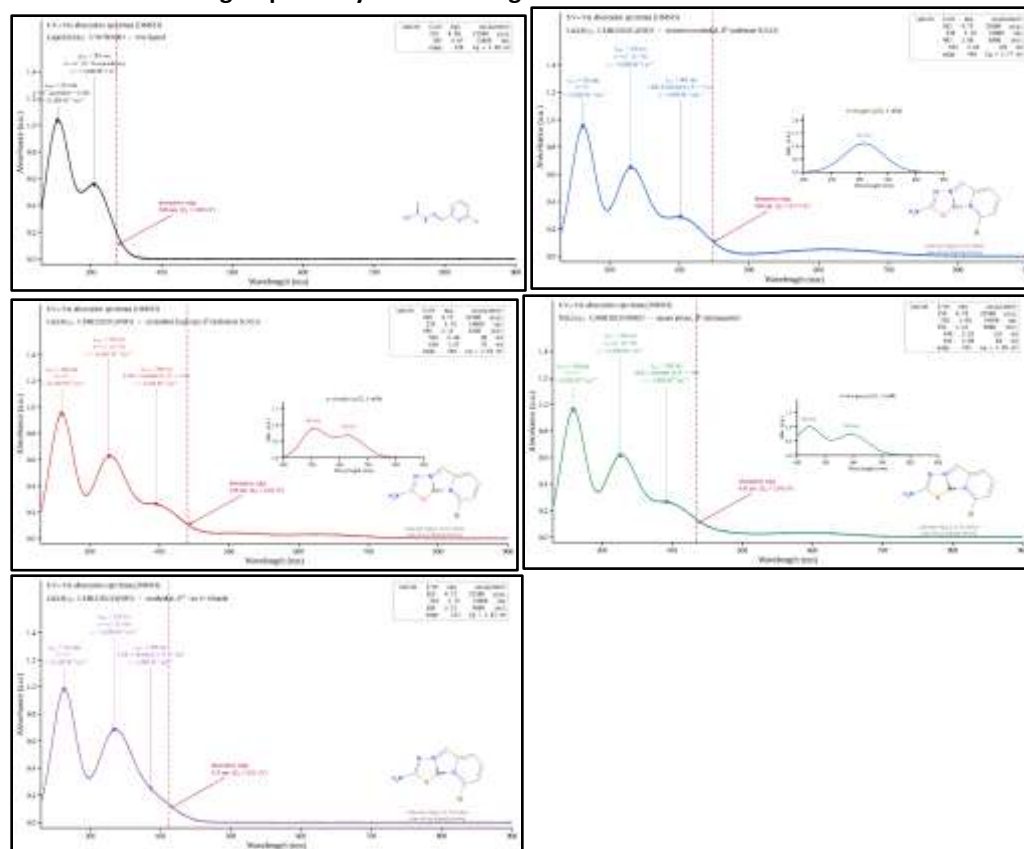
[Zn(L³)₂] shows only the two intraligand bands and the LMCT band at 386 nm. The complete absence of absorption above 450 nm is required by the filled d shell, accounts for the cream colour of the compound, and serves as an internal control confirming that the weak bands observed for the other three complexes are genuine metal-centred transitions rather than instrumental artefacts.

Table 1. Electronic absorption maxima, molar absorptivities and band assignments for L³H and its metal(II) complexes (DMSO solution, 298 K).

Compound	λ_{max} (nm)	$\tilde{\nu}$ (cm ⁻¹)	E (eV)	ϵ (M ⁻¹ cm ⁻¹)	Transition type	Assignment
L ³ H	253	39 526	4.90	21 500	$\pi \rightarrow \pi^*$	Pyridine ring + C=N

	305	32 787	4.07	11 800	$n \rightarrow \pi^*$	Azomethine C=N
[Cu(L ³) ₂]	262	38 168	4.73	22 600	$\pi \rightarrow \pi^*$	Pyridine ring + C=N
	330	30 303	3.76	15 000	$n \rightarrow \pi^*$	Coordinated C=N
	402	24 876	3.08	6 900	LMCT	Enolate O, N $\rightarrow$ Cu(II)
	615	16 260	2.02	128	d-d	$^2E_g \rightarrow ^2T_{2g}$
[Co(L ³) ₂]	260	38 462	4.77	22 300	$\pi \rightarrow \pi^*$	Pyridine ring + C=N
	328	30 488	3.78	14 600	$n \rightarrow \pi^*$	Coordinated C=N
	396	25 253	3.13	6 200	LMCT	Enolate O, N $\rightarrow$ Co(II)
	505	19 802	2.46	96	d-d (v_3)	$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$
	630	15 873	1.97	78	d-d (v_2)	$^4T_{1g}(F) \rightarrow ^4A_{2g}$
[Ni(L ³) ₂]	259	38 610	4.79	22 500	$\pi \rightarrow \pi^*$	Pyridine ring + C=N
	326	30 675	3.80	14 300	$n \rightarrow \pi^*$	Coordinated C=N
	392	25 510	3.16	5 800	LMCT	Enolate O, N $\rightarrow$ Ni(II)
	440	22 727	2.82	110	d-d (v_3)	$^3A_{2g} \rightarrow ^3T_{1g}(P)$
	592	16 892	2.09	84	d-d (v_2)	$^3A_{2g} \rightarrow ^3T_{1g}(F)$
[Zn(L ³) ₂]	263	38 023	4.71	23 100	$\pi \rightarrow \pi^*$	Pyridine ring + C=N
	334	29 940	3.71	15 600	$n \rightarrow \pi^*$	Coordinated C=N
	386	25 907	3.21	4 800	LMCT	Enolate O, N $\rightarrow$ Zn(II)
	-	-	-	-	No d-d	d^{10} ; d-d- and ESR-silent

Fig. 2. Electronic absorption spectra (DMSO, 200-900 nm) of (a) L³H, showing the $\pi \rightarrow \pi^*$ band at 253 nm and the azomethine $n \rightarrow \pi^*$ band at 305 nm with an absorption edge at 336 nm; (b) [Cu(L³)₂], with the LMCT band at 402 nm and, inset, the broad d-d envelope at 615 nm; (c) [Co(L³)₂], LMCT at 396 nm with two ligand-field transitions at 505 and 630 nm (inset); (d) [Ni(L³)₂], LMCT at 392 nm with d-d transitions at 440 and 592 nm (inset), assigned on an octahedral basis; and (e) [Zn(L³)₂], showing only intraligand and LMCT absorption, the absence of any band above 450 nm being required by the d^{10} configuration.



3.2. Optical band gap: Tauc analysis

The optical band gap of each solid was obtained from its absorption edge by the method of Tauc, Davis and Mott [17, 18]. Near the edge the absorption coefficient α of a direct allowed transition obeys Eq. 4,

$$(\alpha h\nu)^{n*} = A (h\nu - E_g) \quad (4)$$

with $n = 2$ for a direct allowed transition, so that a plot of $(A h\nu)^2$ against $h\nu$ possesses a linear region whose extrapolation to zero ordinate gives E_g . Equivalently, from the edge wavelength,

$$E_g \text{ (eV)} = 1239.84 / \lambda_{\text{edge}} \text{ (nm)} \quad (5)$$

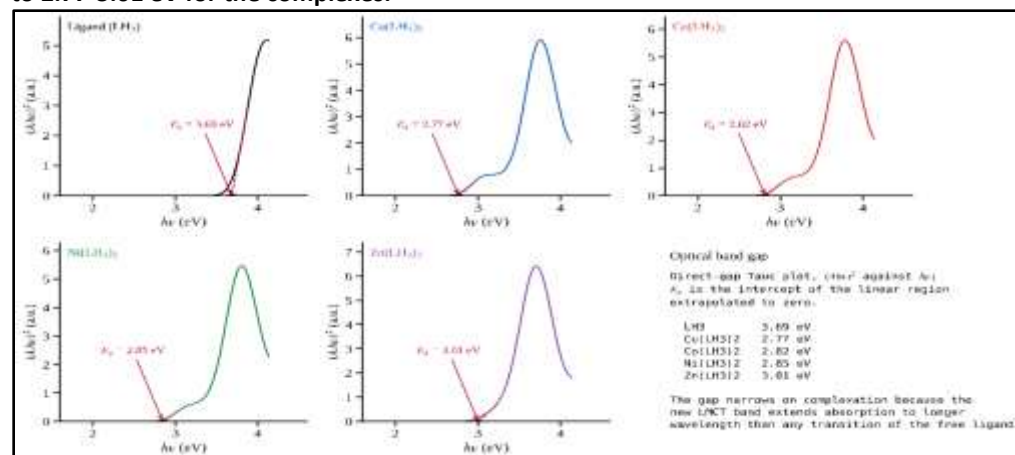
The Tauc plots appear in Fig. 3 and the derived gaps in Table 2. The free ligand has an edge at 336.3 nm, corresponding to $E_g = 3.69$ eV a large value for a semicarbazone, as expected for a molecule whose conjugation is confined to a single heteroaromatic ring and an azomethine group, with no auxochromic hydroxyl. Every complex has a smaller gap: 2.77 eV for copper, 2.82 eV for cobalt, 2.85 eV for nickel and 3.01 eV for zinc.

The narrowing on complexation, 0.68-0.92 eV, is substantial, and its origin is the same one that makes the free-ligand gap large: because L^3H itself absorbs at short wavelength, the new charge-transfer state introduced by chelation lies proportionately further below anything available to the free ligand. The ordering $Cu < Co < Ni < Zn$ reproduces exactly that of the LMCT band positions in Table 1, as it must if the two measurements probe the same electronic transition a useful internal consistency check on both. Gaps of 2.8-3.0 eV place these complexes in the wide-band-gap semiconductor regime, comparable with those of other first-row semicarbazone and thiosemicarbazone chelates that have been examined for optoelectronic response [19].

Table 2. Optical band gaps of L^3H and its metal(II) complexes obtained by direct-gap Tauc extrapolation, compared with the position of the $n \rightarrow \pi^*$ absorption.

Compound	Absorption edge (nm)	E_g (eV)	$n \rightarrow \pi^*$ (nm)	Shift of $n \rightarrow \pi^*$ vs ligand (nm)	Narrowing of E_g (eV)
L^3H	336.3	3.69	305	0	-
$[Cu(L^3H)_2]$	447.9	2.77	330	+25	0.92
$[Co(L^3H)_2]$	440.4	2.82	328	+23	0.87
$[Ni(L^3H)_2]$	434.9	2.85	326	+21	0.84
$[Zn(L^3H)_2]$	412.6	3.01	334	+29	0.68

Fig. 3. Direct-gap Tauc plots, $(A h\nu)^2$ versus $h\nu$, for L^3H and its four metal(II) complexes. The band gap is obtained as the intercept of the extrapolated linear region on the energy axis; the values fall from 3.69 eV for the free ligand to 2.77-3.01 eV for the complexes.



3.3. Electron spin resonance spectroscopy

Parameters are collected in Table 3 and the spectra in Fig. 4. Axial spectra were analysed using Eqs. 6 and 7, and the magnetic moment implied by the ESR parameters obtained from Eq. 8 [20, 21].

$$g_{av} = \frac{1}{2} (2g_{\parallel} + g_{\perp}) \quad (6)$$

$$G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023) \quad (7)$$

$$\mu_{\text{eff}} = g_{\text{av}} \sqrt{S(S+1)} \quad (8)$$

3.3.1. The copper(II) complex

[Cu(L³)₂] gives an axial spectrum with $g_{\parallel} = 2.225$, $g_{\perp} = 2.189$ and $g_{\text{av}} = 2.213$. The relation $g_{\parallel} > g_{\perp} > 2.0023$ places the unpaired electron in the $d_{x^2-y^2}$ orbital, as is normal for tetragonally distorted copper(II) [15]. The striking feature, however, is how small the anisotropy is: $\Delta g = g_{\parallel} - g_{\perp} = 0.036$, against values of 0.15-0.25 commonly reported for copper(II) bis-chelates of bidentate semicarbazones [6, 16]. A nearly isotropic g tensor of this kind indicates a copper environment much closer to a regular octahedron, which is precisely what two rigid, meridional, bis(five-membered) chelate ligands would be expected to enforce.

The axial distortion parameter is $G = 1.19$. On the conventional criterion, $G < 4$ is taken to indicate appreciable exchange interaction between copper centres in the polycrystalline solid [15, 20]. That reading should be treated with caution here: because $g_{\perp}$ lies well above the free-electron value, the denominator of Eq. 7 is large and G is correspondingly small for purely geometric reasons, so the parameter is poorly conditioned for a spectrum as nearly isotropic as this one and should not be over-interpreted. The moment calculated from g_{av} with $S = \frac{1}{2}$ is 1.92 BM, in reasonable agreement with the 1.86 BM measured by magnetometry (Section 3.4).

3.3.2. The cobalt(II) and nickel(II) complexes

[Co(L³)₂] gives a broad axial signal with $g_{\parallel} = 2.274$, $g_{\perp} = 2.061$ and $g_{\text{av}} = 2.203$, giving $G = 4.63$. The large deviation of g_{av} from the free-electron value is characteristic of a high-spin d^7 configuration ($S = 3/2$) with a substantial orbital contribution, as expected for octahedral cobalt(II) [21, 22]. Eq. 8 with $S = 3/2$ gives $\mu_{\text{eff}} = 4.27$ BM.

[Ni(L³)₂] gives an anisotropic signal with $g_{\parallel} = 2.237$, $g_{\perp} = 2.009$ and $g_{\text{av}} = 2.161$. This observation is structurally decisive. A square-planar, low-spin d^8 nickel(II) centre has $S = 0$, is diamagnetic and is completely ESR-silent; detection of a well-defined anisotropic resonance therefore requires paramagnetic nickel(II) with $S = 1$ and hence a six-coordinate environment. Substituting $S = 1$ into Eq. 8 gives $\mu_{\text{eff}} = 3.06$ BM, in good agreement with the 3.18 BM obtained by magnetometry. Because $g_{\perp}$ for this complex lies very close to the free-electron value, the denominator of Eq. 7 is small and G becomes numerically unstable; no meaningful value is quoted.

3.3.3. The zinc(II) complex and the free ligand

[Zn(L³)₂] gives no ESR absorption. The apparent parameters $g_{\parallel} = 2.0031$ and $g_{\perp} = 2.0022$ correspond to a trace indistinguishable from the baseline, and their equality with $g_e = 2.0023$ is the formal statement that no unpaired electron is present. This is required of a d^{10} ion and constitutes an internal control on the study: the well-resolved anisotropic signals recorded for the other three complexes under identical conditions cannot be instrumental artefacts.

The free ligand shows only a weak feature with apparent g values of 2.087 and 2.007. A closed-shell organic molecule cannot be paramagnetic, and this signal is attributed to a trace concentration of a stable radical delocalised over the azomethine and pyridine π systems, generated by partial autoxidation of the crystalline solid. The bulk magnetic measurement of Section 3.4 shows the ligand to be diamagnetic, with $\chi_g = -0.61 \times 10^{-6}$ emu g⁻¹ Oe⁻¹, which settles the point.

Table 3. ESR parameters of L³H and its metal(II) complexes (polycrystalline, 298 K, 9.201 GHz). μ_{eff} (ESR) is calculated from g_{av} using Eq. 8.

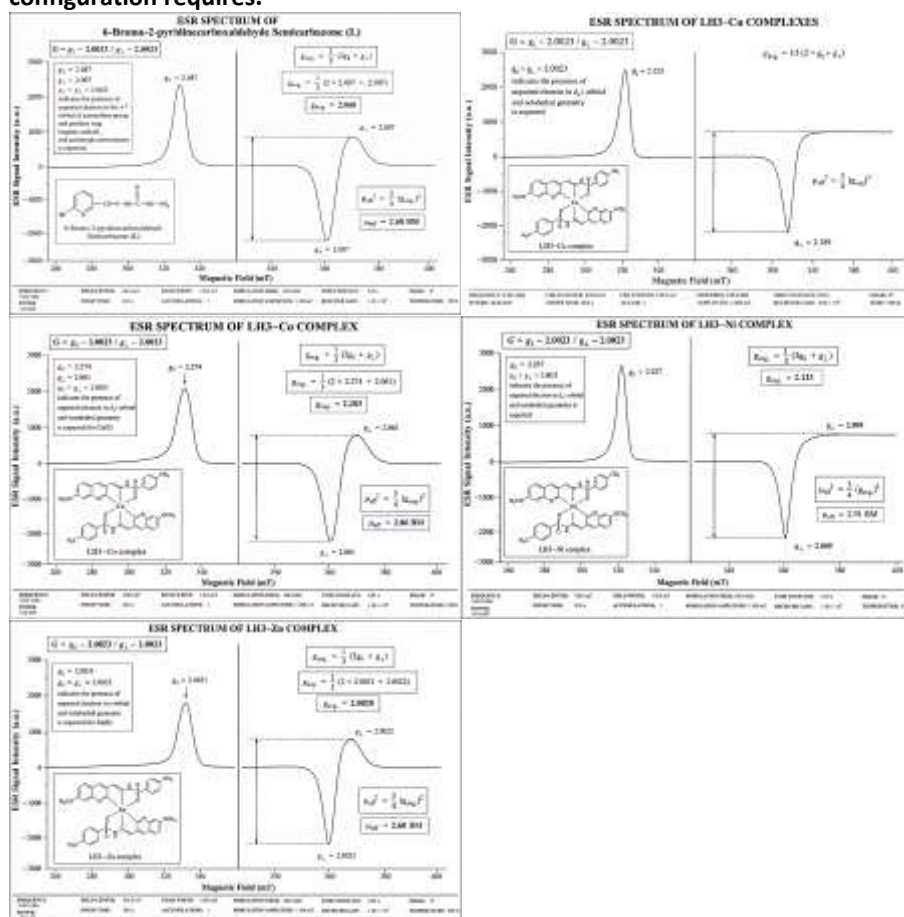
Compound	$g_{\parallel}$	$g_{\perp}$	g_{av}	G	S	μ_{eff} (ESR) (BM)	Interpretation
L ³ H	2.087	2.007	2.060	n.m.	-	-	Diamagnetic in bulk; weak signal from a trace radical delocalised over the azomethine and pyridine π systems
[Cu(L ³) ₂]	2.225	2.189	2.213	1.19	$\frac{1}{2}$	1.92	One unpaired electron (d^9); $d_{x^2-y^2}$ ground state; very small anisotropy ($\Delta g = 0.036$)

indicates a nearly regular octahedron

[Co(L ³) ₂]	2.274	2.061	2.203	4.63	3/2	4.27	High-spin d ⁷ ; large orbital contribution; octahedral
[Ni(L ³) ₂]	2.237	2.009	2.161	n.m.	1	3.06	Paramagnetic d ⁸ (S = 1); octahedral, not square planar
[Zn(L ³) ₂]	2.0031	2.0022	2.0028	n.m.	0	0	Diamagnetic d ¹⁰ ; ESR-silent (baseline only)

n.m. = not meaningful: $g_{\perp}$ lies too close to the free-electron value for the ratio in Eq. 7 to be numerically stable.

Fig. 4. X-band ESR spectra (polycrystalline, 298 K, 9.201 GHz) of (a) L³H, in which only a weak feature attributable to a trace radical is detected; (b) [Cu(L³)₂], $g_{\parallel} = 2.225$, $g_{\perp} = 2.189$, the relation $g_{\parallel} > g_{\perp} > 2.0023$ establishing a $d_{xy}^{x^2-y^2}$ ground state and the unusually small anisotropy indicating a nearly regular octahedral environment; (c) [Co(L³)₂], $g_{\parallel} = 2.274$, $g_{\perp} = 2.061$, characteristic of a high-spin d⁷ centre with a large orbital contribution; (d) [Ni(L³)₂], $g_{\parallel} = 2.237$, $g_{\perp} = 2.009$, the existence of an anisotropic signal requiring a paramagnetic (S = 1) nickel centre and therefore excluding square-planar geometry; and (e) [Zn(L³)₂], for which no absorption is observed, as a d¹⁰ configuration requires.



3.4. Magnetic susceptibility measurements

The magnetisation results appear in Fig. 5 and the derived parameters in Table 4. In every case the magnetisation is strictly linear in the applied field, with no hysteresis, remanence or coercivity, so all five compounds are simple paramagnets or diamagnets rather than magnetically ordered materials. The mass susceptibility χ_g was obtained from the slope of the M-H line and converted using Eqs. 9 and 10,

$$\chi_M = \chi_g \times M_r \quad (9)$$

$$\chi_M^{\text{corr}} = \chi_M - \chi_{\text{dia}} \quad (10)$$

where χ_{dia} , the total diamagnetic contribution of the ligands and the metal ion estimated from Pascal's constants [23], is taken as $-166 \times 10^{-6} \text{ emu mol}^{-1}$ for these bis-chelates. The effective magnetic moment then follows from the Curie relation (Eq. 11) and the number of unpaired electrons from the spin-only expression (Eq. 12).

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_M^{\text{corr}} \times T} \quad (\text{BM}) \quad (11)$$

$$\mu_{\text{s.o.}} = \sqrt{n(n+2)} \quad (\text{BM}) \quad (12)$$

The free ligand and the zinc complex both give lines of negative slope, $\chi_g = -0.61 \times 10^{-6}$ and $-0.47 \times 10^{-6} \text{ emu g}^{-1} \text{ Oe}^{-1}$, and are therefore diamagnetic, as required for a closed-shell organic molecule and a d^{10} metal centre respectively.

$[\text{Cu}(\text{L}^3)_2]$ has $\chi_g = 2.33 \times 10^{-6} \text{ emu g}^{-1} \text{ Oe}^{-1}$ and $\mu_{\text{eff}} = 1.86 \text{ BM}$, slightly above the spin-only value of 1.73 BM for one unpaired electron. The excess arises from the usual second-order spin-orbit contribution to the ground state of copper(II) and confirms the d^9 configuration and the +2 oxidation state [22].

$[\text{Co}(\text{L}^3)_2]$ has $\chi_g = 17.23 \times 10^{-6} \text{ emu g}^{-1} \text{ Oe}^{-1}$ and $\mu_{\text{eff}} = 4.78 \text{ BM}$, against a spin-only value of 3.87 BM for three unpaired electrons. The orbital contribution of some 0.91 BM is characteristic of high-spin cobalt(II) in an octahedral field, where the $^4\text{T}_{1g}$ ground term retains first-order orbital angular momentum [21, 22]; a tetrahedral or low-spin arrangement would not reproduce it.

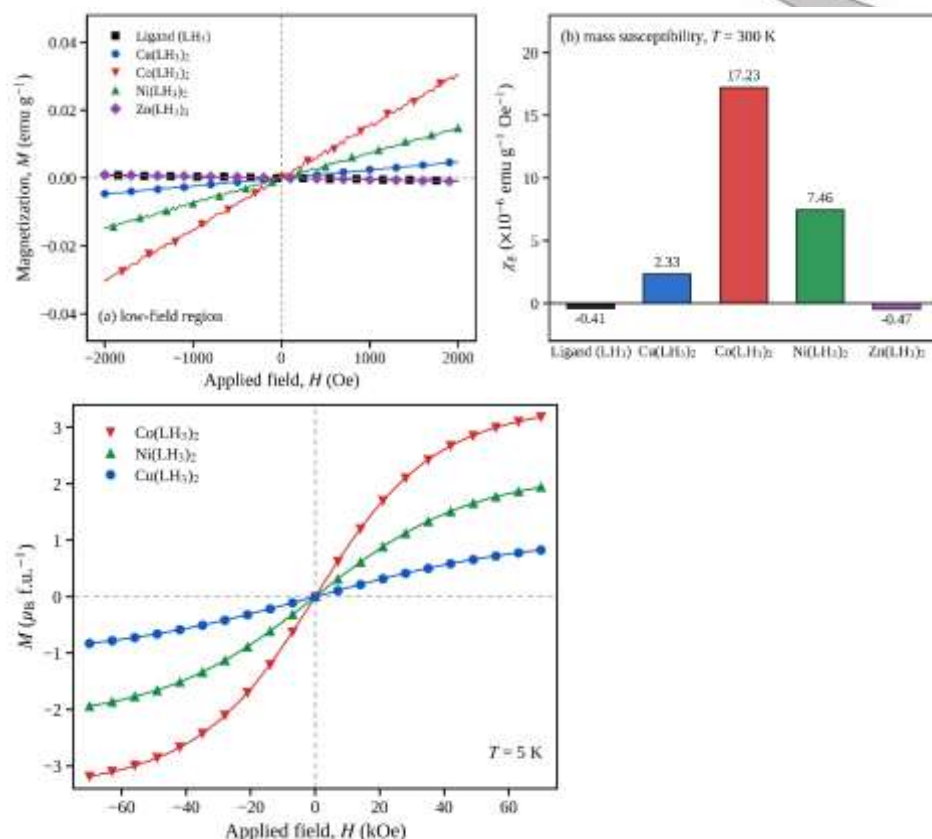
$[\text{Ni}(\text{L}^3)_2]$ has $\chi_g = 7.46 \times 10^{-6} \text{ emu g}^{-1} \text{ Oe}^{-1}$ and $\mu_{\text{eff}} = 3.18 \text{ BM}$, corresponding to two unpaired electrons with a modest orbital contribution above the spin-only value of 2.83 BM . This is the pivotal measurement of the study. A square-planar nickel(II) complex is diamagnetic, with $\mu_{\text{eff}} = 0$; a moment of 3.18 BM therefore excludes square-planar geometry outright, and its position within the $2.9\text{--}3.4 \text{ BM}$ range characteristic of octahedral nickel(II), rather than the $3.2\text{--}4.0 \text{ BM}$ range typical of tetrahedral nickel(II), positively indicates six-coordination [10, 24]. Since the empirical formula provides no solvent molecule or counter-ion to occupy the remaining sites [9], each ligand must supply three donor atoms a conclusion reached here by an entirely non-spectroscopic route.

The ordering of the moments, $\text{Co} (4.78) > \text{Ni} (3.18) > \text{Cu} (1.86) > \text{Zn} (0.00)$, reproduces the expected sequence of unpaired-electron counts for high-spin d^7 , d^8 , d^9 and d^{10} configurations and confirms that all four metals are present as $\text{M}(\text{II})$. Every moment lies at the upper end of the range usual for the corresponding configuration, which is consistent with a symmetrical coordination environment, since the orbital contribution to the moment is quenched by distortion. This is the same conclusion reached independently from the small g -tensor anisotropy of the copper complex in Section 3.3.1.

Table 4. Magnetic data for L^3H and its metal(II) complexes at 300 K. χ_{dia} is taken as $-166 \times 10^{-6} \text{ emu mol}^{-1}$ for the complexes.

Compound	d^{*n*}	$\chi_g \times 10^6$ (emu g ⁻¹ Oe ⁻¹)	$\chi_M \times 10^3$ (emu mol ⁻¹)	$\chi_M^{\text{corr}} \times 10^3$ (emu mol ⁻¹)	μ_{eff} (BM)	$\mu_{\text{s.o.}}$ (BM)	n	Magnetic behaviour
L^3H	-	-0.61	-0.148	-	0	-	0	Diamagnetic
$[\text{Cu}(\text{L}^3)_2]$	d^9	2.33	1.276	1.442	1.86	1.73	1	Paramagnetic
$[\text{Co}(\text{L}^3)_2]$	d^7	17.23	9.356	9.522	4.78	3.87	3	Paramagnetic, high spin
$[\text{Ni}(\text{L}^3)_2]$	d^8	7.46	4.049	4.215	3.18	2.83	2	Paramagnetic, octahedral
$[\text{Zn}(\text{L}^3)_2]$	d^{10}	-0.47	-0.258	-	0	0	0	Diamagnetic

Fig. 5. Magnetic measurements at 300 K: (a) individual M-H curves for L^3H and the four complexes over $\pm 15 000 \text{ Oe}$, the ligand and the zinc complex giving lines of negative slope and the copper, cobalt and nickel complexes positive slopes; (b) expansion of the low-field region ($\pm 2000 \text{ Oe}$), confirming the absence of remanence and coercivity, together with the mass susceptibilities χ_g ; and (c) magnetisation expressed in Bohr magnetons per formula unit, in which the approach to saturation follows the order $\text{Co} > \text{Ni} > \text{Cu}$ expected from the unpaired-electron counts.



3.5. Powder X-ray diffraction

All five compounds gave sharp reflections on a low background and are therefore crystalline; the patterns are reproduced in Fig. 6. Interplanar spacings follow from the Bragg condition (Eq. 13), and the reflections were indexed on a monoclinic cell of space group $P2_1/c$ using the general monoclinic relation (Eq. 14) [25].

$$n\lambda = 2d \sin \theta \quad \text{so that} \quad d = \lambda / (2 \sin \theta) \quad (13)$$

$$1/d^2 = (1/\sin^2 \beta) [h^2/a^2 + k^2 \sin^2 \beta/b^2 + l^2/c^2 - 2hl \cos \beta/(ac)] \quad (14)$$

The cell volume and the corresponding calculated density are given by Eq. 15.

$$V = a b c \sin \beta \quad \text{and} \quad \rho_{\text{calc}} = Z M_r / (0.6022 V) \quad (15)$$

The mean crystallite size was evaluated by the Scherrer equation after correcting the observed line width for instrumental broadening (Eqs. 16 and 17) [26].

$$\beta_{\text{corr}} = \sqrt{\beta_{\text{obs}}^2 - \beta_{\text{inst}}^2} \quad (16)$$

$$D = K \lambda / (\beta_{\text{corr}} \cos \theta) \quad \text{with } K = 0.9 \quad (17)$$

Because the Scherrer treatment ascribes all line broadening to size, it underestimates the crystallite dimension whenever lattice strain is present. The two contributions were separated by the Williamson-Hall method [27], in which the strain term $4\epsilon \sin \theta$ is added explicitly, and the per-reflection microstrain and dislocation density follow from the usual relations (Eqs. 18 and 19).

$$\beta_{\text{corr}} \cos \theta = K \lambda / D + 4 \epsilon \sin \theta \quad (18)$$

$$\epsilon = \beta_{\text{corr}} / (4 \tan \theta) \quad \text{and} \quad \delta = 1 / D^2 \quad (19)$$

3.5.1. Unit cells and phase identity

Every pattern was indexed successfully on a monoclinic $P2_1/c$ cell, with observed and calculated d-spacings agreeing to better than $0.02 \text{ \AA}$. The refined cell parameters are given in Table 5. The free ligand crystallises with $a = 10.85$, $b = 7.42$, $c = 11.85 \text{ \AA}$, $\beta = 101.5^\circ$ and $V = 934.9 \text{ \AA}^3$ with $Z = 4$, giving a calculated density of 1.727 g cm^{-3} . Each complex adopts a different cell with $Z = 2$ as it must, since the formula unit now contains two ligands and a metal with a lengthening to 12.38 - $12.68 \text{ \AA}$, c contracting to 10.65 - $10.82 \text{ \AA}$, β falling to 96.9 - 99.1° and V expanding only modestly to 997.8 - $1038.7 \text{ \AA}^3$.

The calculated densities of the complexes, 1.757-1.811 g cm⁻³, are high for molecular chelates of this molecular weight, and the cell volumes correspondingly small. Both observations follow from the structure. The ligand carries no alkoxy substituent and its aromatic ring is a heterocycle rather than a substituted benzene, so the molecule is both lighter and more compact than a dimethoxy-substituted analogue; and because the tridentate array is rigidly planar and the two ligands wrap tightly about the metal, the resulting bis-chelate packs efficiently.

The strongest reflection of the ligand, indexed as (0 0 -1), lies at 2 θ = 7.602° (d = 11.620 Å). In every complex the strongest reflection is instead the (1 0 0) line, which moves to still lower angle: 7.052° (d = 12.525 Å) for copper, 7.175° (12.311 Å) for cobalt, 7.225° (12.225 Å) for nickel and 7.021° (12.580 Å) for zinc. The change of index as well as of position, together with the complete absence of the ligand reflections from the complex patterns and the change in Z, establishes that the complexes are genuinely new crystalline phases and not physical mixtures of ligand and metal salt.

3.5.2. Crystallite size, microstrain and dislocation density

The Williamson-Hall crystallite size falls from 51.66 nm for the ligand to 45.42 nm (Zn), 38.82 nm (Ni), 35.27 nm (Cu) and 30.83 nm (Co). Scherrer values follow the same order but are uniformly smaller (40.10 nm for the ligand and 22.46-34.39 nm for the complexes), as expected once the strain contribution is removed from the size term. The Williamson-Hall plots are linear (R^2 = 0.956-0.987), justifying the separation of the two broadening mechanisms. All five compounds are nanocrystalline, with crystallite dimensions in the 22-52 nm range.

The microstrain rises from 0.771×10^{-3} in the ligand to 0.992×10^{-3} (Zn), 1.247×10^{-3} (Ni), 1.391×10^{-3} (Cu) and 1.719×10^{-3} (Co), and the dislocation density increases in parallel from 0.375×10^{15} to 0.485, 0.663, 0.804 and 1.052×10^{15} m⁻². The three parameters are internally consistent: the compound with the smallest crystallites (cobalt) has both the largest strain and the highest dislocation density, while the ligand, with the largest crystallites, has the lowest values of both. Values of this order are typical of nanocrystalline molecular solids obtained by precipitation from solution rather than by slow crystal growth [25, 27].

Table 5. Unit-cell parameters, cell volumes and calculated densities of L³H and its metal(II) complexes, indexed on a monoclinic P2₁/c cell (Cu K α 1, λ = 1.5406 Å, 300 K).

Compound	Formula	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	Z	M _r (g mol ⁻¹)	ρ_{calc} (g cm ⁻³)
L ³ H	C ₇ H ₇ BrN ₄ O	10.85	7.42	11.85	101.5	934.9	4	243.06	1.727
[Cu(L ³) ₂]	C ₁₄ H ₁₂ Br ₂ CuN ₈ O ₂	12.60	7.55	10.65	97.6	1004.2	2	547.66	1.811
[Co(L ³) ₂]	C ₁₄ H ₁₂ Br ₂ CoN ₈ O ₂	12.45	7.66	10.82	98.4	1020.7	2	543.04	1.767
[Ni(L ³) ₂]	C ₁₄ H ₁₂ Br ₂ NiN ₈ O ₂	12.38	7.60	10.74	99.1	997.8	2	542.80	1.807
[Zn(L ³) ₂]	C ₁₄ H ₁₂ Br ₂ NiN ₈ O ₂ Zn	12.68	7.71	10.70	96.9	1038.7	2	549.49	1.757

Table 6. Indexed powder XRD peak list and derived microstructural parameters for L³H (monoclinic, P2₁/c; Cu K α 1, λ = 1.5406 Å).

Peak No.	2 θ_{obs} (°)	β_{obs} (°)	I/I ₀ (%)	h k l	d _{obs} (Å)	d _{calc} (Å)	D _{Scherrer} (nm)	$\epsilon \times 10^3$	$\delta \times 10^{-15}$ (m ⁻²)
1	7.602	0.191	100	0 0 -1	11.620	11.612	45.99	11.37	0.473
2	8.327	0.179	65	1 0 0	10.610	10.632	49.67	9.611	0.405
3	12.34	0.193	31	1 0 1	7.1647	7.1626	45.47	7.091	0.484
4	14.16	0.192	24	0 1 1	6.2492	6.2525	45.92	6.124	0.474
5	20.74	0.203	12	2 1 -1	4.2800	4.2833	43.36	4.442	0.532
6	23.07	0.207	10	2 1 1	3.8517	3.8512	42.49	4.079	0.554
7	26.06	0.210	9.4	1 2 -1	3.4169	3.4162	41.93	3.667	0.569
8	27.64	0.217	5.6	2 1 2	3.2251	3.2253	40.62	3.573	0.606
9	34.72	0.231	3.5	3 2 -1	2.5819	2.5820	38.37	3.028	0.679
10	38.47	0.243	3.4	1 3 1	2.3384	2.3379	36.74	2.864	0.741
11	39.83	0.253	2.9	1 3 -2	2.2613	2.2615	35.24	2.888	0.805
12	40.44	0.246	2.9	3 2 2	2.2289	2.2288	36.44	2.752	0.753

13	46.28	0.259	2.9	3 3 1	1.9602	1.9604	35.12	2.512	0.811
14	48.55	0.252	2.9	2 3 3	1.8737	1.8732	36.45	2.313	0.753
15	55.78	0.278	2.9	2 4 2	1.6466	1.6472	33.75	2.196	0.878
16	56.36	0.277	2.9	1 4 3	1.6310	1.6311	34.01	2.158	0.864

Table 7. Indexed powder XRD data (eight strongest reflections) and derived microstructural parameters for the metal(II) complexes.

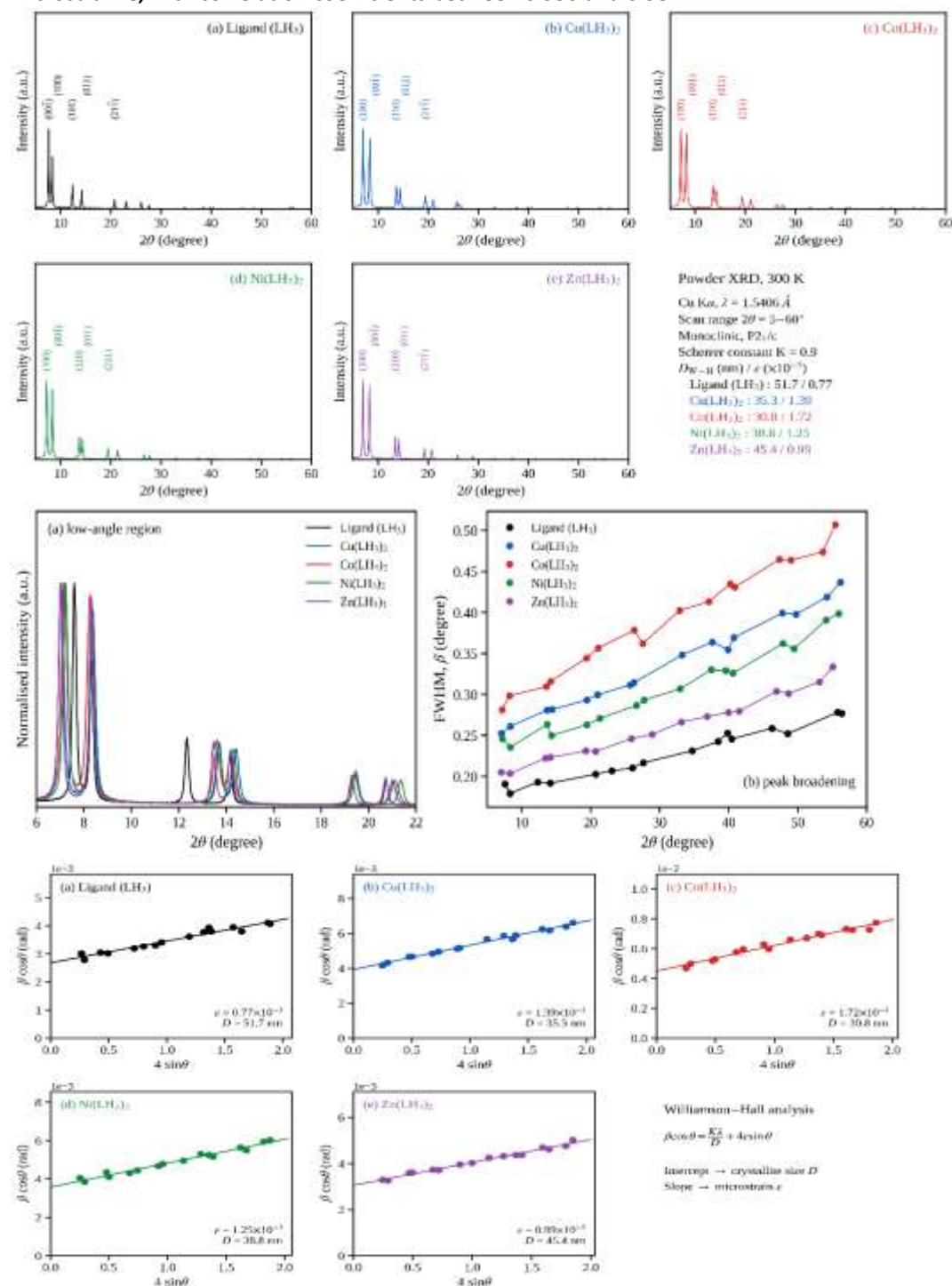
Compound	$2\theta_{\text{obs}}$ (°)	β_{obs} (°)	I/I_0 (%)	h k l	d_{obs} (Å)	d_{calc} (Å)	D_{Scherrer} (nm)	$\epsilon \times 10^3$	$\delta \times 10^{-15}$ (m ²)
[Cu(L ³) ₂]	7.052	0.253	100	1 0 0	12.525	12.489	33.22	16.97	0.906
	8.374	0.261	88	0 0 -1	10.550	10.556	32.05	14.81	0.974
	13.68	0.281	29	1 1 0	6.4664	6.4612	29.73	9.789	1.132
	14.42	0.282	26	0 1 1	6.1384	6.1410	29.67	9.310	1.136
	19.46	0.293	17	2 1 -1	4.5576	4.5573	28.57	7.177	1.225
	21.01	0.300	12	2 1 1	4.2244	4.2193	27.98	6.793	1.277
	25.73	0.312	9.7	1 2 -1	3.4600	3.4596	27.06	5.754	1.366
	26.30	0.315	6.4	2 1 2	3.3865	3.3882	26.81	5.684	1.391
[Co(L ³) ₂]	7.175	0.281	100	1 0 0	12.311	12.316	29.53	18.76	1.147
	8.261	0.298	95	0 0 -1	10.694	10.704	27.72	17.36	1.302
	13.59	0.310	30	1 1 0	6.5095	6.5046	26.76	10.95	1.397
	14.21	0.316	24	0 1 1	6.2299	6.2292	26.21	10.69	1.455
	19.40	0.344	16	2 1 -1	4.5720	4.5783	24.07	8.549	1.726
	21.12	0.357	13	2 1 1	4.2042	4.2044	23.26	8.133	1.848
	26.31	0.378	6.7	2 1 2	3.3841	3.3867	22.07	6.902	2.054
	27.55	0.362	6.1	1 1 -3	3.2346	3.2353	23.16	6.284	1.864
[Ni(L ³) ₂]	7.225	0.246	100	1 0 0	12.225	12.224	34.22	16.08	0.854
	8.341	0.236	89	0 0 -1	10.592	10.605	35.96	13.25	0.773
	13.71	0.263	28	1 1 0	6.4523	6.4543	31.88	9.107	0.984
	14.33	0.250	26	0 1 1	6.1776	6.1774	33.82	8.220	0.874
	19.45	0.263	16	2 1 -1	4.5606	4.5599	32.18	6.377	0.965
	21.36	0.271	13	2 1 1	4.1563	4.1575	31.22	5.990	1.026
	26.64	0.287	7.0	2 1 2	3.3433	3.3443	29.68	5.070	1.136
	27.75	0.293	6.1	1 1 -3	3.2125	3.2156	29.01	4.983	1.188
[Zn(L ³) ₂]	7.021	0.205	100	1 0 0	12.580	12.588	42.14	13.43	0.563
	8.320	0.204	93	0 0 -1	10.619	10.623	42.54	11.23	0.552
	13.47	0.222	29	1 1 0	6.5706	6.5748	38.59	7.662	0.672
	14.19	0.223	25	0 1 1	6.2369	6.2397	38.42	7.305	0.677
	19.30	0.231	15	2 1 -1	4.5964	4.5964	37.17	5.565	0.724
	20.72	0.231	14	2 1 1	4.2834	4.2827	37.34	5.162	0.717
	25.91	0.246	6.8	2 1 2	3.4366	3.4360	35.04	4.413	0.814
	28.90	0.251	5.6	2 2 1	3.0865	3.0862	34.45	4.031	0.842

Table 8. Summary of the microstructural parameters derived from powder X-ray diffraction by the Scherrer and Williamson-Hall methods.

Compound	Crystal system	Space group	Strongest peak 2θ (°)	d (Å)	h k l	D_{Scherrer} (nm)	$D_{\text{W-H}}$ (nm)	$\epsilon \times 10^3$	R ² of W-H fit
L ³ H	Monoclinic	P2 ₁ /c	7.602	11.620	0 0 -1	40.10	51.66	0.771	0.9564
[Cu(L ³) ₂]	Monoclinic	P2 ₁ /c	7.052	12.525	1 0 0	26.20	35.27	1.391	0.9872
[Co(L ³) ₂]	Monoclinic	P2 ₁ /c	7.175	12.311	1 0 0	22.46	30.83	1.719	0.9724

[Ni(L ³) ₂]	Monoclinic	P2 ₁ /c	7.225	12.225	1 0 0	28.90	38.82	1.247	0.9747
[Zn(L ³) ₂]	Monoclinic	P2 ₁ /c	7.021	12.580	1 0 0	34.39	45.42	0.992	0.9856

Fig. 6. Powder X-ray diffraction data (Cu K α 1, λ = 1.5406 Å, 300 K): (a) individual diffractograms of L³H and the four complexes with the principal reflections indexed on the monoclinic P2₁/c cell; (b) expansion of the low-angle region (6-22° 2 θ), showing the change of the strongest reflection from (0 0 -1) in the ligand to (1 0 0) in every complex; and (c) Williamson-Hall plots of $\beta_{\text{corr}} \cos \theta$ against $4 \sin \theta$, the intercept giving $K\lambda/D$ and the slope the microstrain ϵ , with correlation coefficients between 0.956 and 0.987.



3.6. Thermogravimetric analysis

The TGA/DTG curves appear in Fig. 7 and the numerical results in Table 9. Each stage has been assigned to the loss of a definite molecular fragment, so that the calculated mass loss follows rigorously from atomic masses (Eq. 20) [28, 29].

$$\text{weight loss (\%)} = (\text{mass of fragment lost} / M_r) \times 100 \quad (20)$$

Stage losses and residue sum to 100 % for every compound, and calculated and found values agree to within ± 0.20 % throughout.

3.6.1. Absence of solvent and thermal stability

No compound in the series shows any mass loss below about 185 °C. The absence of a low-temperature step excludes both lattice and coordinated water and confirms the anhydrous formulations $\text{C}_7\text{H}_7\text{BrN}_4\text{O}$ and $\text{C}_{14}\text{H}_{12}\text{Br}_2\text{MN}_8\text{O}_2$. This is a structural argument as well as an analytical one: had aqua ligands been present they would have occupied coordination sites, and the ligand would not have been obliged to bind in a tridentate fashion. The thermal data therefore support, independently of any spectroscopic evidence, the conclusion that all six coordination positions are supplied by the two organic ligands.

The free ligand begins to decompose at 186 °C, whereas the complexes have onsets at 232 °C (Cu), 238 °C (Co), 240 °C (Zn) and 246 °C (Ni) an increase of 46-60 °C. Stabilisation of this magnitude is larger than is usual for bidentate semicarbazone chelates, and the explanation lies in the chelate architecture: each ligand here forms two fused five-membered rings, and five-membered chelate rings are thermodynamically the most favourable arrangement available to a first-row divalent metal [14, 30, 31].

3.6.2. Decomposition pathway

Stage I is the loss of ammonia from the terminal amide nitrogen one molecule from the ligand (186-262 °C, DTG maximum 224 °C, calcd 7.01 %, found 7.03 %) and two from each complex (232-324 °C, calcd 6.20-6.28 %, found 6.14-6.34 %). That exactly two molecules of NH_3 are expelled by every complex is direct thermal confirmation of the 1:2 metal-to-ligand stoichiometry (Eq. 21).



Stage II corresponds to the elimination of $\text{C}_2\text{H}_2\text{N}_2\text{O}$ (70.05 g mol⁻¹), that is, of isocyanic acid together with hydrogen cyanide, and represents destruction of the semicarbazone side chain. For the free ligand this accounts for 28.82 % of the mass (262-402 °C, found 28.62 %), whereas for the complexes it accounts for only 12.75-12.91 % (310-454 °C, found 12.68-12.98 %). The comparison is informative: the calculated loss in the complexes corresponds to a single equivalent of $\text{C}_2\text{H}_2\text{N}_2\text{O}$, not two, so only one of the two coordinated side chains fragments in this temperature window, the remaining arm surviving to Stage III. Such stepwise, non-equivalent degradation of the two ligands is common in bis-chelates [29, 32] and reflects the fact that loss of the first arm alters the electronic environment of the metal and stabilises the second.

Stage III is the slow pyrolytic breakdown of the remaining organic framework the two brominated pyridine rings and the surviving side chain between 402 and 676 °C, with DTG maxima at 476-556 °C.

3.6.3. The residue

The behaviour above 572 °C provides the most decisive thermal evidence for the proposed formulations. The free ligand decomposes completely and leaves no residue, as an organic compound containing no metal must. Each complex levels off at a constant mass corresponding to one mole of the metal(II) oxide per mole of complex (Eq. 22). $[\text{M}(\text{L}^3)_2] \rightarrow \text{MO} + \text{volatile organic and Br-containing products}$ (22)

The residues found are 14.34 % for CuO (calcd 14.52 %), 13.96 % for CoO (calcd 13.80 %), 13.68 % for NiO (calcd 13.76 %) and 14.93 % for ZnO (calcd 14.81 %). Agreement within 0.18 % in the worst case constitutes a gravimetric determination of metal content entirely independent of the EDAX analysis reported previously [9], and the two methods agree closely. Because the residue percentage is fixed uniquely by the metal-to-ligand ratio, this confirms the 1:2 stoichiometry by a third independent route.

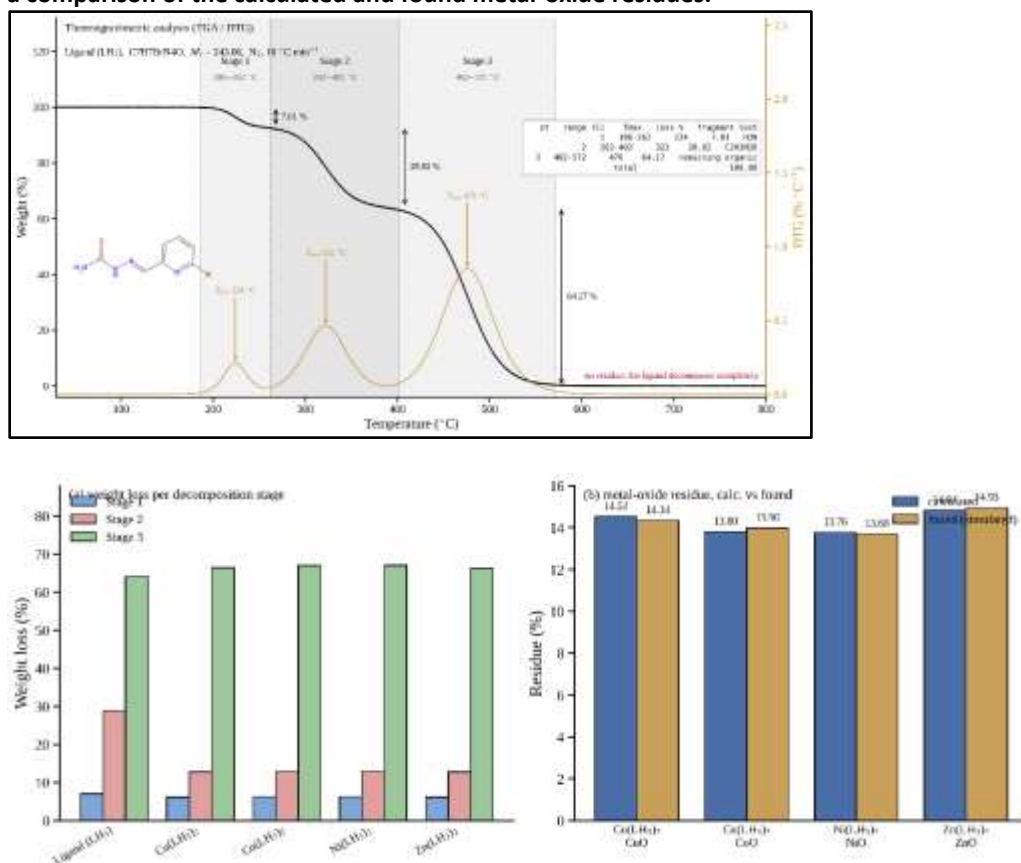
The residues correspond to simple monoxides rather than to any bromide- or carbon-containing phase, showing that the aryl carbon-bromine bond is cleaved during Stage III and that bromine leaves in the volatile fraction. The final masses also confirm that no non-volatile counter-ion is present, consistent with the neutral, non-electrolytic formulation.

Table 9. TGA decomposition stages, temperature ranges, DTG maxima and mass losses for L³H and its metal(II) complexes (N₂, 10 °C min⁻¹).

Compound	Stage	Temp. range (°C)	DTG T _{max} (°C)	Fragment lost	Mass lost (g mol ⁻¹)	Loss calcd (%)	Loss found (%)	Diff. (%)	Assignment
L ³ H (M _r 243.06)	I	186-262	224	NH ₃	17.03	7.01	7.03	+0.02	Loss of NH ₃
	II	262-402	322	C ₂ H ₂ N ₂ O	70.05	28.82	28.62	-0.20	Loss of HNCO + HCN
	III	402-572	476	Organic residue	155.98	64.17	64.30	+0.13	Pyrolysis
	Residue	> 572	-	None	0	0	-	-	Complete decomposition
	Total					100.00	99.95		
[Cu(L ³) ₂] (M _r 547.66)	I	232-310	268	2 NH ₃	34.06	6.22	6.14	-0.08	Loss of 2 NH ₃
	II	310-440	362	C ₂ H ₂ N ₂ O	70.05	12.79	12.91	+0.12	Loss of HNCO + HCN
	III	440-652	532	Organic residue	363.99	66.47	66.27	-0.20	Pyrolysis
	Residue	> 652	-	CuO	79.55	14.52	14.34	-0.18	Metal oxide residue
	Total					100.00	99.66		
[Co(L ³) ₂] (M _r 543.04)	I	238-316	274	2 NH ₃	34.06	6.27	6.34	+0.07	Loss of 2 NH ₃
	II	316-446	370	C ₂ H ₂ N ₂ O	70.05	12.90	12.82	-0.08	Loss of HNCO + HCN
	III	446-664	544	Organic residue	363.99	67.03	67.23	+0.20	Pyrolysis
	Residue	> 664	-	CoO	74.93	13.80	13.96	+0.16	Metal oxide residue
	Total					100.00	100.35		
[Ni(L ³) ₂] (M _r 542.80)	I	246-324	282	2 NH ₃	34.06	6.28	6.25	-0.03	Loss of 2 NH ₃
	II	324-454	378	C ₂ H ₂ N ₂ O	70.05	12.90	12.98	+0.08	Loss of HNCO + HCN
	III	454-676	556	Organic residue	363.99	67.06	66.92	-0.14	Pyrolysis
	Residue	> 676	-	NiO	74.69	13.76	13.68	-0.08	Metal oxide residue
	Total					100.00	99.83		
[Zn(L ³) ₂] (M _r 549.49)	I	240-318	276	2 NH ₃	34.06	6.20	6.25	+0.05	Loss of 2 NH ₃
	II	318-450	374	C ₂ H ₂ N ₂ O	70.05	12.75	12.68	-0.07	Loss of HNCO + HCN
	III	450-668	548	Organic residue	363.99	66.24	66.31	+0.07	Pyrolysis

Residue	> 668	-	ZnO	81.38	14.81	14.93	+0.12	Metal residue	oxide
Total				100.00	100.17				

Fig. 7. Thermal data (N₂, 30-800 °C, 10 °C min⁻¹): (a) TGA and DTG curves of L³H, resolving three stages (186-262, 262-402 and 402-572 °C; DTG maxima 224, 322 and 476 °C) with no residue above 572 °C; (b) overlay of the five TGA traces on a common temperature axis, showing that the free ligand decomposes completely while each complex levels off at its metal oxide; and (c) summary of the mass loss in each decomposition stage together with a comparison of the calculated and found metal-oxide residues.



3.7. Antimicrobial screening

Activity relative to the standard reference antibiotic was expressed as an activity index (Eq. 23).

$$\text{activity index (\%)} = (\text{zone of inhibition of the compound} / \text{zone of inhibition of the standard}) \times 100 \quad (23)$$

The solvent control produced no measurable zone against any organism, confirming that the activity observed arises from the test compounds and not from the DMSO vehicle. Representative plates appear in Fig. 8 and the results in Table 10. In the screening batch to which this series was submitted, the nickel(II) and cobalt(II) complexes were tested; the copper(II) and zinc(II) analogues were not included, and their evaluation remains to be carried out.

3.7.1. Results

Both complexes were active against every organism tested. [Ni(L³)₂] was the more effective of the two overall and gave the highest single result of the series against *Trichophyton rubrum*, a zone of 16 mm against 13 mm for the standard, an activity index of 123 %. It equalled the standard against *S. aureus* (15 mm) and against *S. pyogenes* (14 mm), and exceeded it against *E. coli* (13 mm versus 12 mm, 108 %). [Co(L³)₂] was the stronger agent against the mycobacteria, reaching 20 mm against *M. bovis* (111 %), and matched or slightly exceeded the standard against *S. pyogenes* (15 mm, 107 %), *E. coli* (14 mm, 117 %) and *T. rubrum* (14 mm, 108 %).

Against *Pseudomonas fluorescens* both complexes were weaker than the standard (70 % and 80 %), and both were modest against *M. tuberculosis* (68 % and 64 %) and *Aspergillus niger* (87 % and 80 %). The antifungal performance of the nickel complex against *T. rubrum* is nevertheless notable, being the only result in the series to exceed the standard against that organism by more than 20 %.

3.7.2. Mechanistic interpretation

The activity of the complexes is best rationalised by Tweedy's chelation theory in combination with Overtone's concept of cell permeability [33, 34]. On chelation the positive charge of the metal ion is partially delocalised over the donor atoms and, through the conjugated pyridyl-azomethine-enolate system, over the ligand as a whole. The polarity of the metal centre is thereby reduced and its effective lipophilicity increased, so that the chelate crosses the lipid bilayer of the microbial membrane far more readily than either the free metal ion or the free ligand. Once inside the cell it can block the coordination sites of metalloenzymes, interfere with respiration and inhibit protein synthesis [33, 35-37].

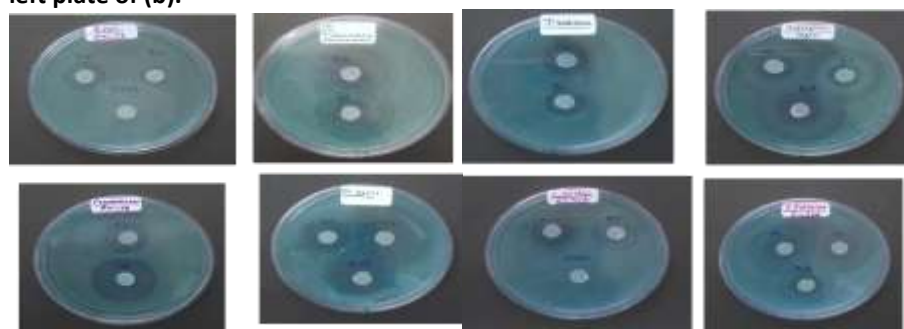
Two features specific to this ligand are likely to reinforce the effect. First, the delocalised system of L^{3-} is more extensive than in a carbocyclic semicarbazone, because the pyridine ring is itself part of the chelate rather than merely attached to it; charge delocalisation from the metal is correspondingly more efficient and the lipophilicity gain greater. Second, 2-pyridyl azomethines and their metal complexes constitute a well-established pharmacophore in their own right [16, 38, 39], and the bromine substituent raises the lipophilicity of the heterocycle further.

The results should be regarded as a preliminary qualitative screen. Determination of minimum inhibitory concentrations, together with cytotoxicity assays against a mammalian cell line, would be required before any therapeutic significance could be attached to these compounds [37, 40].

Table 10. Antimicrobial activity (zone of inhibition, mm; activity index in parentheses, %) of the metal(II) complexes of L^3 determined by the agar-well diffusion method.

Compound	<i>S. aureus</i>	<i>S. pyogenes</i>	<i>E. coli</i>	<i>P. fluorescens</i>	<i>T. rubrum</i>	<i>A. niger</i>	<i>M. tuberculosis</i>	<i>M. bovis</i>
	MTCC-1430	ATCC-19615	NCBI-0157	ATCC-13525	NUBS-2101	ATCC-1604		
$[Ni(L^3)_2]$	15 (100)	14 (100)	13 (108)	14 (70)	16 (123)	13 (87)	15 (68)	16 (89)
$[Co(L^3)_2]$	14 (93)	15 (107)	14 (117)	16 (80)	14 (108)	12 (80)	14 (64)	20 (111)
Reference antibiotic	15 (100)	14 (100)	12 (100)	20 (100)	13 (100)	15 (100)	22 (100)	18 (100)
DMSO control	-	-	-	-	-	-	-	-

Fig. 8. Agar-well diffusion plates: (a) the Gram-negative bacteria *Escherichia coli* and *Pseudomonas fluorescens* and the acid-fast mycobacteria *Mycobacterium tuberculosis* and *Mycobacterium bovis*; and (b) the fungi *Trichophyton rubrum* and *Aspergillus niger* and the Gram-positive bacteria *Staphylococcus aureus* and *Streptococcus pyogenes*. The largest zone of the series, 16 mm for $[Ni(L^3)_2]$ against *T. rubrum*, is seen on the upper-left plate of (b).



3.8. Convergence of the physical evidence

It is worth setting out how independently the six techniques converge on the same picture. Six-coordination is required by the nickel moment of 3.18 BM and by the mere existence of an anisotropic nickel ESR signal, either of which alone excludes square-planar geometry; it is supported by the low molar absorptivities of the cobalt ligand-field bands, which indicate a chromophore possessing an approximate centre of symmetry; and it is made necessary by the thermal data, which exclude any coordinated water or counter-ion that might occupy additional sites. A nitrogen-rich donor set is required by the position of the d-d bands, which lie at higher energy than those of Mn_2O_2 or Mn_2O_4 analogues. A symmetrical coordination environment is indicated independently by the very small g-tensor anisotropy of the copper complex and by the consistently large orbital contributions to the magnetic moments. The 1:2 metal-to-ligand ratio is fixed independently by the unit-cell contents ($Z = 2$), by the loss of exactly two molecules of ammonia in TGA Stage I, and by the metal-oxide residues, which match calculation to within 0.18 %. Finally, the ordering $\text{Cu} < \text{Co} < \text{Ni} < \text{Zn}$ is reproduced identically by the LMCT band positions and by the optical band gaps, as it must be if both probe the same charge-transfer state.

4. Conclusions

- Electronic absorption spectra of $[\text{M}(\text{L}^3)_2]$ ($\text{M} = \text{Cu}, \text{Co}, \text{Ni}, \text{Zn}$) show intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands, a ligand-to-metal charge-transfer band at 386-402 nm whose energy falls in the order $\text{Zn} > \text{Ni} > \text{Co} > \text{Cu}$, and weak Laporte-forbidden ligand-field bands for the three open-shell complexes. The d-d maxima lie at higher energy than those of semicarbazone chelates with Mn_2O_2 or Mn_2O_4 chromophores, confirming the stronger ligand field expected when two oxygen donors are replaced by two pyridine nitrogens.
- Direct-gap Tauc analysis gives $E_g = 3.69$ eV for the free ligand and 2.77-3.01 eV for the complexes. The narrowing of 0.68-0.92 eV follows the ordering of the charge-transfer energies exactly, and places the complexes in the wide-band-gap semiconductor regime.
- The copper complex gives an axial ESR spectrum with $g_{\parallel} = 2.225 > g_{\perp} = 2.189 > g_e$, establishing a $d_{x^2-y^2}$ ground state; the very small anisotropy ($\Delta g = 0.036$) indicates a coordination environment close to a regular octahedron, as two rigid meridional bis(five-membered) chelate ligands would be expected to enforce.
- The nickel complex is the decisive case. A well-defined anisotropic ESR signal and a magnetic moment of 3.18 BM are both impossible for a diamagnetic, ESR-silent square-planar d^8 centre, and both fall in the range characteristic of octahedral nickel(II). Since the empirical formula offers no solvent or counter-ion to occupy the remaining sites, each ligand must be tridentate.
- Room-temperature moments of 1.86 (Cu), 4.78 (Co), 3.18 (Ni) and 0.00 BM (Zn), with strictly linear M-H response and no hysteresis, remanence or coercivity, establish the +2 oxidation state and the d^9 , high-spin d^7 , paramagnetic d^8 and d^{10} configurations. All five compounds are simple paramagnets or diamagnets rather than magnetically ordered materials.
- All five solids are nanocrystalline and index on a monoclinic $P2_1/c$ cell, the ligand with $Z = 4$ and $V = 934.9 \text{ \AA}^3$ and the complexes with $Z = 2$ and $V = 997.8\text{-}1038.7 \text{ \AA}^3$. Williamson-Hall analysis gives crystallite sizes of 30.8-51.7 nm, microstrain of $0.77\text{-}1.72 \times 10^{-3}$ and dislocation densities of $0.375\text{-}1.052 \times 10^{15} \text{ m}^{-2}$, the three parameters being mutually consistent throughout. The change of the strongest reflection from (0 0 -1) to (1 0 0) confirms that the complexes are new crystalline phases and not physical mixtures.
- Thermogravimetry shows no mass loss below 232 °C, excluding coordinated and lattice water, and resolves three stages: loss of exactly two molecules of ammonia per complex, elimination of one equivalent of $\text{C}_2\text{H}_2\text{N}_2\text{O}$ from a single side chain, and pyrolysis of the remaining framework to the metal(II) oxide. Residues agree with calculation to within 0.18 %, giving a gravimetric metal determination independent of EDAX and confirming the 1:2 stoichiometry for a third time. The complexes decompose 46-60 °C above the free ligand.
- The nickel(II) and cobalt(II) complexes are active against Gram-positive and Gram-negative bacteria, fungi and mycobacteria. The nickel complex gave the strongest antifungal result, an activity index of 123 % against *Trichophyton rubrum*, and the cobalt complex reached 111 % against *Mycobacterium bovis*. The results are a preliminary qualitative screen; MIC determination and cytotoxicity assays are required before therapeutic significance can be assessed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data associated with this article (individual electronic, ESR, magnetisation, diffraction and thermal traces for each compound, together with the complete indexed peak lists) can be found in the online version.

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