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FORMATION CONDITIONS AND FT–IR CHARACTERIZATION OF THE QUERCETIN–COPPER(II)–1,10-PHENANTHROLINE MIXED-LIGAND COMPLEX

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Abstract: *The solvent-free interaction of quercetin, copper(II) acetate monohydrate, and 1,10-phenanthroline in a 1:1:1 molar ratio was investigated. Trituration at room temperature for 15–30 min produced a dark-brown 11;2N product. Its FT–IR spectrum contained phenanthroline-related bands at 1587, 843, and 718 cm^{-1} and tentative Cu–O and Cu–N vibrations at 646 and 432 cm^{-1}. The observed spectral changes support the formation of a mixed-ligand coordination product. However, additional physicochemical analyses are required to establish its exact composition and coordination geometry.*

Keywords: *quercetin, copper(II), 1,10-phenanthroline, mixed-ligand complex, solid-state synthesis, FT–IR spectroscopy, coordination bond.*

KVERSETIN–MIS(II)–1,10-FENANTROLIN ARALASH LIGANDLI KOMPLEKSINING HOSIL BO‘LISH SHAROITLARI VA FT–IR TAVSIFI

Annotatsiya: *Kversetin, mis(II) asetat monogidrat va 1,10-fenantrolinning 1:1:1 molyar nisbatdagi erituvchisiz o‘zaro ta’siri o‘rganildi. Reagentlar xona haroratida 15–30 daqiqa trituratsiya qilinib, to‘q jigarrang 11;2N mahsuloti olindi. Uning FT–IR spektrida fenantrolin skeletiga xos 1587, 843 va 718 cm^{-1} hamda ehtimoliy Cu–O va Cu–N bog‘lariga tegishli 646 va 432 cm^{-1} signallar aniqlandi. Spektral o‘zgarishlar aralash ligandli koordinatsion mahsulot hosil bo‘lganini qo‘llab-quvvatlaydi. Biroq kompleksning aniq tarkibi va geometriyasini tasdiqlash uchun qo‘shimcha fizik-kimyoviy tahlillar zarur.*

Kalit so‘zlar: *kversetin, mis(II), 1,10-fenantrolin, aralash ligandli kompleks, qattiq fazali sintez, FT–IR spektroskopiya, koordinatsion bog‘.*

УСЛОВИЯ ОБРАЗОВАНИЯ И FT–IR-ХАРАКТЕРИСТИКА СМЕШАННОЛИГАНДНОГО КОМПЛЕКСА КВЕРЦЕТИН–МЕДЬ(II)–1,10-ФЕНАНТРОЛИН

Аннотация: *Изучено взаимодействие кверцетина, моногидрата ацетата меди(II) и 1,10-фенантролина в мольном соотношении 1:1:1 без использования растворителя. Тритурация реагентов при комнатной температуре в течение 15–30 мин привела к образованию тёмно-коричневого продукта 11;2N. В его FT–IR-спектре обнаружены характерные для фенантролина полосы 1587, 843 и 718 $см^{-1}$, а также предположительно относящиеся к колебаниям Cu–O и Cu–N сигналы 646 и 432 $см^{-1}$. Спектральные изменения подтверждают вероятность образования смешаннолигандного координационного продукта. Для установления точного состава и геометрии комплекса необходимы дополнительные физико-химические исследования.*

Ключевые слова: *кверцетин, медь(II), 1,10-фенантролин, смешаннолигандный комплекс, твердофазный синтез, FT–IR-спектроскопия, координационная связь.*

INTRODUCTION

Quercetin (3,3′,4′,5,7-pentahydroxyflavone) is a polyphenolic flavonoid whose carbonyl, phenolic, and catechol functions can participate in metal-ion binding. Its coordination chemistry is important because chelation changes the distribution of electron density in the flavonoid skeleton, shifts redox potentials, and can modify solubility, radical-scavenging behaviour, and interactions with biomolecular targets [1–4]. Copper(II) is particularly relevant: it is a biologically essential, redox-active d^9 ion and forms stable O-donor chelates with flavonoids. At the same time, its spectral behaviour is sensitive to the number and type of donor atoms in the first coordination sphere.

The quercetin molecule offers several possible metal-binding sites. The most frequently proposed sites are the 3-hydroxy/4-carbonyl system of the C ring, the 5-hydroxy/4-carbonyl system, and the 3′,4′-dihydroxy catechol group of the B ring. Which site is occupied depends on the copper salt, pH, solvent, deprotonation conditions, stoichiometry, water content, and the presence of an additional ligand [2–4]. Consequently, a change in colour or a single shifted infrared band cannot, on its own, define a molecular structure. Comparison with free ligands, binary metal–ligand products, and published ternary complexes is required.

1,10-Phenanthroline (phen) is a rigid bidentate N,N-donor ligand. Its two ring nitrogens readily bind Cu(II), while the fused aromatic framework gives a set of intense and readily recognisable vibrations in the 1600–700 cm^{-1} region. Combining quercetin and phenanthroline around Cu(II) creates an O,N mixed-donor environment. Such heteroleptic copper complexes have been investigated as antioxidant, anticancer, antimicrobial, osteogenic, and angiogenic candidates [5–10]. From a synthetic perspective, a mixed-ligand complex may also be obtained with less solvent and shorter reaction time than conventional reflux procedures by using mechanochemical or triturative activation [6].

The present work had two objectives. The first was to describe operational formation conditions for a quercetin–Cu(II)–phenanthroline product using equimolar, solvent-free trituration. The second was to assess whether the FT–IR spectrum of the product contains a combined set of quercetin-derived, phenanthroline-derived, and metal–donor features that is distinguishable from the available binary and comparison samples. The analysis deliberately separates observations from structural inference: the term «mixed-ligand complex» is used as a working coordination model, while formula and geometry are treated as hypotheses pending independent confirmation.

LITERATURE REVIEW

Infrared spectroscopy is widely used as an initial test of flavonoid coordination. Free quercetin commonly shows a broad O–H envelope in the 3500–3200 cm^{-1} region, a strong 4-carbonyl band around 1665–1666 cm^{-1}, aromatic C=C vibrations near 1610, 1560, and 1510 cm^{-1}, C–OH deformation near 1379 cm^{-1}, and C–O/C–O–C vibrations between approximately 1320 and 1160 cm^{-1} [4,5]. The exact values vary with hydration, crystallinity, sampling mode, and hydrogen bonding. Catauro et al. reported quercetin bands at 3406/3283, 1666, 1610, 1560, 1510, 1379, 1317, 1263, 1200, and 1165 cm^{-1} [5]. These values provide a useful reference for the present discussion, but they are not substituted for measurements of a free-quercetin batch under identical instrumental conditions.

In binary Cu(II)–quercetin systems, coordination is usually inferred from displacement or broadening of the carbonyl and phenolic C–O bands and the appearance of low-frequency metal–oxygen vibrations. Bukhari et al. combined spectrophotometric and IR evidence to support binding through the carbonyl oxygen and a neighbouring deprotonated hydroxyl group [4]. Because ring vibrations are strongly coupled, however, reported assignments are not fully uniform. A band in the 620–650 cm^{-1} region can support Cu–O bonding, but it may overlap with ligand deformation modes or inorganic residues. The most defensible interpretation therefore considers a pattern of changes rather than a single peak.

The literature contains several routes to quercetin–Cu(II)–diimine complexes. Gençkal et al. prepared $[Cu(queH{-}1)Cl(phen)]\cdot 2.5H_2O$ in methanolic solution by first reacting quercetin with base and $CuCl_2$ and then adding phenanthroline under reflux [7]. Their reported IR spectrum included 1639 cm^{-1} for C=O, 1600 cm^{-1} for C=C, 1589 cm^{-1} for C=N, 1362 cm^{-1} for C–OH, 1273 cm^{-1} for C–O–C, phenanthroline skeletal bands at 846 and 721 cm^{-1}, and low-frequency features at 652 and 433 cm^{-1} assigned to Cu–O and Cu–N, respectively. This detailed assignment is particularly useful for evaluating a product formed by a different route.

Andelescu et al. obtained heteroleptic Cu(II) and Zn(II) quercetin complexes with bipyridine or phenanthroline [8]. For the phenanthroline-containing Cu(II) derivative, the reported IR maxima included 3433, 3081, 1641, 1611, 1520, 1487, 1429, 1276, 1167, 844, and 720 cm^{-1}. The cluster at 1520, 1429, 1276, 1167, 844, and 720 cm^{-1} provides a stringent fingerprint comparison because it includes both high-intensity framework vibrations and the diagnostic out-of-plane modes of phenanthroline. Vimalraj et al. used a sequential methanolic route with $CuSO_4\cdot 5H_2O$, quercetin, and phenanthroline and isolated a dark brown product; their study illustrates that the order of addition and pre-formation of a copper–quercetin species can influence the final material [9].

A solvent-free alternative was reported by Srivastava et al. [6]. Equimolar quercetin, copper(II) acetate, and phenanthroline were triturated at room temperature to afford a dark-brown product. The proposed formula, high yield, elemental composition, and exact IR data in that publication belong to the cited work and cannot be transferred to a new sample without measurement. Nevertheless, the route offers a practical basis for the present synthesis because it minimises solvent use and promotes intimate contact among the solid reactants. The literature IR values for the reported phenanthroline complex—3402, 1612, 1568, 1417, 1266, 1169, 825, and 721 cm^{-1}—serve only as external comparison values.

These reports also define an important interpretive constraint. Free or hydrated phenanthroline itself displays bands close to 1587, 1505, 1422, 1345, 1295, 1185, 1138, 1092, 1036, 987, 853/839, 763/738, and 709 cm^{-1}. Therefore, observation of phenanthroline bands in a product proves its presence but not necessarily its coordination. Evidence for a ternary complex

is strengthened when phenanthroline fingerprints coexist with quercetin-derived changes and new low-frequency metal–donor bands, and when the overall spectrum differs from both the binary quercetin–Cu product and a physical mixture. This pattern-based criterion was adopted here.

MATERIALS AND METHODS

Reagents and sample coding

Quercetin dihydrate, 1,10-phenanthroline, and copper(II) acetate monohydrate were used as the organic ligand, N,N-donor co-ligand, and copper source, respectively. The working method specified equimolar quantities and did not require solvent, base, or an external heating step. The product evaluated as the principal mixed-ligand candidate was coded 11;2N. Two available spectra were treated as comparisons: 11;2, a quercetin-dominant preparation obtained during the same study programme, and Q–Cu, a binary quercetin–copper product. These codes are retained to preserve traceability between the article and the original spectral files.

Table 1

Operational conditions used for solvent-free formation of the 11;2N product

Component or stage	Amount	Molar relation	Operational condition
Quercetin dihydrate	0.338 g	1.00 mmol (1 eq.)	Combined first with phenanthroline
1,10-Phenanthroline	0.180 g	1.00 mmol (1 eq.)	Pre-ground with quercetin for 3–5 min
$Cu(CH_3COO)_2{\cdot}H_2O$	0.200 g	1.00 mmol (1 eq.)	Added after ligand pre-mixing
Trituration	15–30 min	Overall 1:1:1	Dry porcelain mortar; room temperature
Post-treatment	Until dry	—	Air-dried at room temperature; stored dry and protected from light

Solvent-free synthesis

Quercetin dihydrate (0.338 g, 1.00 mmol) and 1,10-phenanthroline (0.180 g, 1.00 mmol) were placed in a clean, dry porcelain mortar and triturated for 3–5 min until a visually homogeneous powder was obtained. Copper(II) acetate monohydrate (0.200 g, 1.00 mmol) was then added. Trituration was continued at room temperature for 15–30 min. During grinding, the initial yellow colour changed to dark brown. The material was dried at room temperature and stored in a dry, light-protected container before FT–IR analysis. No experimental yield, elemental composition, melting point, or isolated molecular formula was available; literature values for similar products were therefore not presented as results of this work.

FT–IR measurement and data treatment

FT–IR spectra were available as exported ATR transmittance files covering approximately 4000–400 cm^{-1} with a data interval of about 1.44 cm^{-1}. The instrument manufacturer/model and nominal spectral resolution were not retained in the exported text metadata and are therefore not inferred. Experimental maxima were identified as local transmittance minima after mild Savitzky–Golay treatment (21-point window, third-order polynomial); the reported positions were checked against the unsmoothed traces. Smoothing was used only to assist consistent peak selection and graphical presentation, not to create or delete spectral features.

Each trace was normalised independently for overlay plots, and vertical offsets were applied to prevent overlap. Because absolute transmittance depends on ATR contact pressure, particle packing, and sample amount, intensity differences between separately recorded solids were not used quantitatively. Interpretation focused on band positions, the presence or absence of diagnostic regions, and similarity to the binary Q–Cu spectrum and published spectra. All assignments below are therefore band-based, and low-frequency Cu–O/Cu–N assignments are explicitly described as tentative.

RESULTS AND DISCUSSION

Macroscopic evidence and role of the formation conditions

The yellow-to-dark-brown change during trituration is consistent with a change in the electronic environment of quercetin and Cu(II). Similar colour changes have been reported for solution-prepared and solid-state quercetin–copper–phenanthroline products [6,8,9]. The observation is useful as a rapid process indicator, but it is not structural proof because copper acetate–quercetin coordination, partial oxidation of quercetin, and Cu(II)–phenanthroline association can each darken the solid. Its significance increases only when evaluated together with the FT–IR profile.

The selected conditions provide three practical controls over product formation. First, a 1:1:1 stoichiometric feed offers one quercetin molecule and one bidentate phenanthroline molecule per copper ion, consistent with a heteroleptic O,N donor set. Second, pre-grinding the two ligands improves their dispersion before the metal salt is introduced and reduces local excess of Cu(II). Third, continued mechanical contact for 15–30 min supplies repeated fracture, mixing, and fresh-surface formation without bulk solvent. The experiment establishes these as operational formation conditions; it does not yet constitute a formal optimisation because time, stoichiometry, humidity, and addition order were not varied systematically.

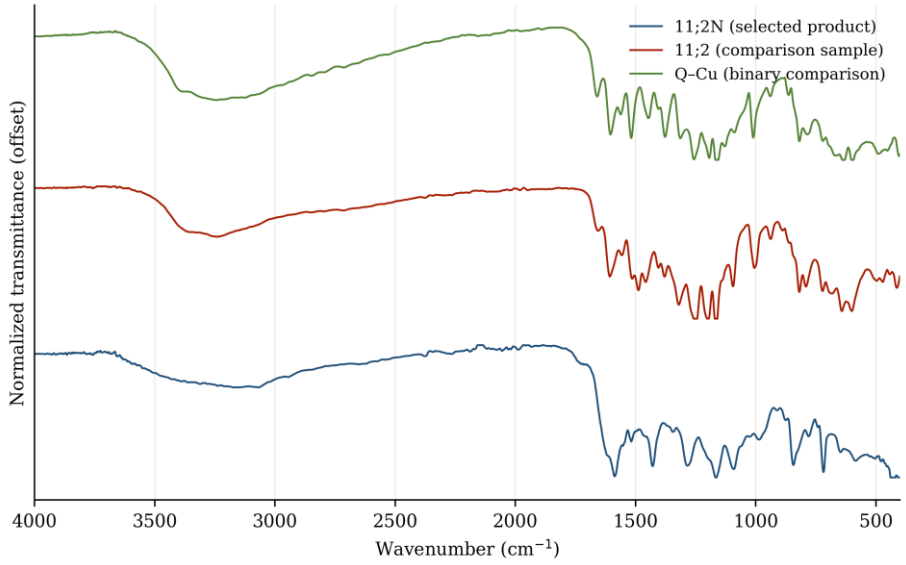


Figure 1. Full-range ATR–FT–IR comparison of the 11;2N product, 11;2 comparison sample, and binary Q–Cu product (normalised and vertically offset).

Comparison with the binary Q–Cu and 11;2 samples

The binary Q–Cu spectrum retained a broad O–H region centred near 3243 cm^{-1} and a resolved carbonyl-region band at 1660 cm^{-1}. Additional maxima occurred at 1604, 1561, 1518, 1446, 1377, 1313, 1257, 1193, 1162, 1129, 1089, 1010, 939, 863, 819, 786, 721, 633, 597, and 490 cm^{-1}. Relative to the literature value of about 1666 cm^{-1} for free quercetin [5], the 1660 cm^{-1} maximum shows only a modest displacement. The 633/597 cm^{-1} features may contain a Cu–O contribution, but the binary spectrum remains dominated by quercetin framework vibrations.

The 11;2 spectrum was likewise quercetin-dominant. It contained bands at 3240, 1656, 1607, 1557, 1514, 1488, 1458, 1405, 1379, 1320, 1249, 1198, 1165, 1094, 1005, 938, 819, 791, 722, 642, 600, 497, 471, and 442 cm^{-1}. The close correspondence of its 1656, 1607, 1379, 1249, 1165, 819, and 600 cm^{-1} features with the Q–Cu profile indicates that 11;2 is not the best spectral representation of the desired ternary product. In particular, the characteristic phenanthroline pair near 843–846 and 718–721 cm^{-1} is not expressed as the same coherent fingerprint seen in the literature ternary complexes.

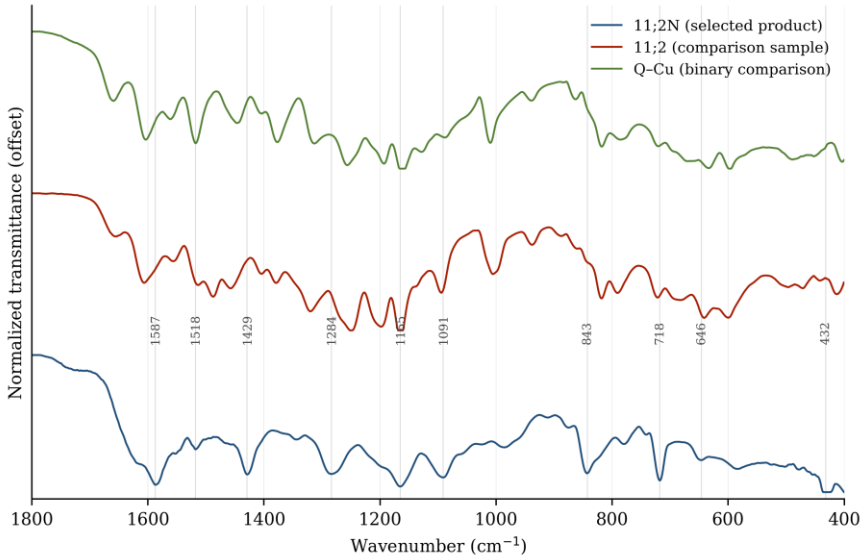


Figure 2. Fingerprint-region comparison (1800–400 cm^{-1}). Vertical guides indicate selected 11;2N maxima used in the mixed-ligand assessment.

Diagnostic features of the 11;2N product

The 11;2N spectrum differed substantially from both comparison traces. Its broad high-frequency feature was centred near 3147 cm^{-1}, and the fingerprint region showed maxima at 1587, 1518, 1429, 1284, 1165, 1091, 985, 843, 780, 718, 646, 585, 503, and 432 cm^{-1}. Several of these bands coincide closely with published heteroleptic Cu(II)–quercetin–phenanthroline spectra. For example, Andelescu et al. reported 1520, 1429, 1276, 1167, 844, and 720 cm^{-1} [8], compared with 1518, 1429, 1284, 1165, 843, and 718 cm^{-1} in 11;2N. The absolute deviations are only 0–8 cm^{-1} for this six-band set, which is within the range expected from different counter-ligands, hydration states, sampling modes, and solid-state packing.

The 1587 cm^{-1} maximum is close to the 1589 cm^{-1} ν(C=N) band reported by Gençkal et al. [7] and to a strong vibration of free phenanthroline. It therefore confirms retention of the phenanthroline framework but is not, by itself, proof of Cu–N coordination. The out-of-plane pair at 843 and 718 cm^{-1} is more informative when considered together: it matches the 846/721 cm^{-1} pair in [Cu(queH−1)Cl(phen)]·2.5H_2O [7] and the 844/720 cm^{-1} pair in the heteroleptic complex reported by Andelescu et al. [8]. The 1284 and 1165 cm^{-1} bands are consistent with coupled C–O–C and ring C–C/C–H modes present in quercetin-containing ternary products.

Low-frequency signals at 646 and 432 cm^{-1} are compatible with metal–donor vibrations. Their positions compare with 652 cm^{-1} (Cu–O) and 433 cm^{-1} (Cu–N) reported by Gençkal et al. [7]. These assignments are marked tentative for two reasons. First, ligand deformation modes can also occur below 700 cm^{-1}. Second, the available free-phenanthroline reference contains features near 450 and 411 cm^{-1}. Coordination is therefore supported by the combined 646/432 cm^{-1} pair and the broader spectral transformation, rather than by either band in isolation.

Table 2

Selected FT–IR bands and comparison with published ligand/complex data

Tentative assignment	Free Q, lit. [5]	Free phen, reference	Q–Cu	11;2	11;2N
ν(O–H)/H-bonded region	3406, 3283	3418	3243	3240	3147
ν(C=O), quercetin	1666	—	1660	1656	not separately resolved
ν(C=C)/ν(C=N)	1610, 1560	1618, 1588, 1562	1604, 1561	1607, 1557	1587
Ring vibration	1510	1505, 1448, 1422	1518, 1446	1514, 1458, 1405	1518, 1429
C–O/C–O–C region	1317, 1263, 1200, 1165	1295, 1185, 1138, 1092	1313, 1257, 1193, 1162, 1089	1320, 1249, 1198, 1165, 1094	1284, 1165, 1091
Phen framework/out-of-plane	933, 820	987, 853/839, 763/738, 709	939, 863, 819, 786, 721	938, 819, 791, 722	985, 843, 780, 718
Possible Cu–O	—	—	633, 597	642, 600	646, 585
Possible Cu–N/low-frequency deformation	—	450, 411	490	497, 471, 442	503, 432

Note: values are in cm^{-1}. «Free phen» values were read from the supplied reference spectrum; they are used as a spectral comparison, not as a newly measured batch in this work.

Assessment of mixed-ligand complex formation

Three independent observations favour 11;2N over 11;2 as the mixed-ligand candidate. First, its profile is not a minor perturbation of the Q–Cu spectrum; the relative prominence and positions of the 1587, 1429, 1284, 1091, 985, 843, 780, and 718 cm^{-1} bands show that the phenanthroline-containing phase dominates the measured ATR contact. Second, the six-band match with the heteroleptic product of Andelescu et al. and the 1589/846/721/652/433 cm^{-1} match with the complex of Gençkal et al. are mutually consistent [7,8]. Third, the 646/432 cm^{-1} pair provides plausible metal–oxygen and metal–nitrogen contributions, whereas the 11;2 sample remains much more similar to the binary Q–Cu material.

The principal counter-observation is the absence of a clearly resolved 1640–1660 cm^{-1} carbonyl maximum in 11;2N. Published complexes generally retain a shifted quercetin carbonyl band, for example at 1639, 1641, or 1612 cm^{-1} [6–8]. In the present trace, the 1660–1600 cm^{-1} interval appears as a sloping/overlapping region rather than a distinct local minimum.

This may result from band overlap, low quercetin contribution at the ATR sampling surface, strong phenanthroline absorption, partial amorphisation, or product heterogeneity. It may also indicate that the measured solid is phenanthroline-rich or contains a Cu–phenanthroline phase in addition to a quercetin species. FT–IR alone cannot distinguish these possibilities.

Accordingly, the strongest defensible conclusion is that 11;2N contains a coordination environment spectrally compatible with a quercetin–Cu(II)–phenanthroline product, but the data do not establish a single pure phase or a unique formula. A working structural model may place Cu(II) between the N,N donor set of phenanthroline and an O,O donor site of mono-deprotonated quercetin, with acetate and/or water completing the coordination sphere. This model agrees with several literature formulations [6–8], yet the identity of the quercetin binding site, the retention of acetate, hydration number, and coordination geometry remain unresolved.

Table 3

Evidence-based classification of the examined spectra

Sample	Dominant spectral character	Evidence for phenanthroline	Interpretive classification
Q–Cu	Quercetin/binary Cu–quercetin	No coherent phen fingerprint	Binary comparison; not a ternary product
11;2	Closely follows Q–Cu	Weak/ambiguous	Quercetin-dominant comparison sample
11;2N	Phenanthroline-rich transformed profile	Strong 1587, 843, 718 cm^{-1} set; low-frequency 646/432 cm^{-1} pair	Strongest mixed-ligand candidate; confirmation required

Analytical limitations and confirmatory work

A publication-grade structural assignment should add at least four checks. UV–Vis spectra should demonstrate changes in the two quercetin $\pi\rightarrow\pi^*$ bands and, if observable, the Cu(II) d–d envelope. EPR should verify Cu(II) and provide information on the ligand field. Elemental analysis or ICP–OES should test the copper-to-organic composition, while high-resolution mass spectrometry can identify solution-phase ions. Powder X-ray diffraction would determine whether the product is a new crystalline or amorphous phase and whether unreacted ligands remain. Thermogravimetric analysis would help quantify water and retained acetate. Finally, the synthesis should be repeated at least three times and accompanied by measured isolated yield and batch-to-batch FT–IR reproducibility.

For optimisation, the 1:1:1 feed should be compared with 1:1:2 and 2:1:1 ligand/metal ratios, and trituration times of 5, 15, 30, and 60 min should be evaluated. A control obtained by simple physical mixing without prolonged grinding is especially important: its spectrum would show which changes arise from mechanical activation rather than arithmetic superposition of the ligands. If a carbonyl band becomes consistently resolved while the 843/718 and 646/432 cm^{-1} pairs are retained, the argument for simultaneous O- and N-donor coordination would become substantially stronger.

CONCLUSIONS

An equimolar quercetin–Cu(II)–1,10-phenanthroline product was prepared under operationally simple, solvent-free conditions by pre-grinding quercetin dihydrate and phenanthroline for 3–5 min, adding copper(II) acetate monohydrate, and continuing trituration for 15–30 min at room temperature. The dark-brown 11;2N product exhibited an FT–IR fingerprint containing 1587, 1518, 1429, 1284, 1165, 1091, 843, 780, 718, 646, 585, 503, and 432 cm^{-1} bands. The 843/718 cm^{-1} phenanthroline pair and the tentative 646/432 cm^{-1} Cu–O/Cu–N pair agree closely with published heteroleptic copper–quercetin–phenanthroline complexes.

Among the spectra examined, 11;2N is the strongest candidate for mixed-ligand complex formation, whereas 11;2 remains quercetin/Q–Cu dominant. Nevertheless, the absence of a separately resolved quercetin carbonyl maximum prevents an unqualified structural claim. The FT–IR data support, but do not conclusively prove, a ternary coordination product. The molecular formula, quercetin binding site, hydration state, and Cu(II) geometry should be established by UV–Vis, EPR, elemental/ICP analysis, mass spectrometry, and powder X-ray diffraction before a definitive structural formulation is assigned.

AUTHOR STATEMENTS

Author contribution. A.R.O. Axmedov: conceptualisation, experimental work, data curation, FT–IR interpretation, visualisation, and preparation of the original manuscript draft.

Conflict of interest. The author declares no conflict of interest related to this study.

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Data availability. The raw ATR–FT–IR files used for the comparative analysis are retained by the author and may be made available with the manuscript.

Ethics statement. The study did not involve human participants, animals, or personal data; ethical approval was therefore not required.

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