Synthesis and characterization of coordination polymers prepared from Cu^{II} and Ni^{II} cyclam perchlorate and carmoisine

Research Article

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Abstract: Reaction of [Cu^{II}(cyclam)](ClO$_4$)$_2$ or [Ni^{II}(cyclam)](ClO$_4$)$_2$ in DMF with aqueous 4-hydroxy-3-(4-sulfonato-1-naphthylazo)naphthalen-1-sulfonate disodium salt (carmoisine) yielded coordination polymers {[Cu^{II}(cyclam)](carmoisine dianion)(H$_2$O)$_5$}n and powder {[Ni^{II}(cyclam)](carmoisine dianion)}$_n$, respectively (cyclam = 1,4,8,11-tetrazacyclotetradecane). They were characterized by powder X-ray diffraction, IR, Raman spectrometry and TGA.

Keywords: Coordination polymer • Cyclam • Self-assembly • Azo dye
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1. Introduction

In coordination polymer/metal organic framework research, networks based on sulfonate ligation are less studied because the coordination of sulfonate anions is relatively weak [1-3]. However, this weaker ligation enables solid state dynamics that are of increasing interest [4-6]. Sulfonate's spherical ligating ability makes *a priori* coordination prediction a challenge, although they appear almost exclusively as monoanions (RSO$_3^{-1}$). This lack of regular inorganic assemblages is not wholly detrimental; new inorganic clusters can form and the structure-directing role of the organic linker can be enhanced.

Sulfonated dyes generally exhibit poor crystal growth making single crystal diffraction studies difficult, although there are a few studies on supramolecular motifs of sulfonated azo dye salts [7-11]. Using synchrotron radiation, Kennedy *et al.* [8] determined the first crystal structure of a red azo lake pigment. Another exception is 7-hydroxy-8-(phenylazo)-1,3 naphthalenedisulfonic acid (Orange G), the salts of which grow as robust crystals. This has led to crystallographic characterization of the

Orange G dianion with both polyatomic organic cations [12] and as its Mg, Ca and Li salts [13]. Kennedy *et al.* [11] synthesized and determined the structures of eight new *s*-block metal compounds of Orange G and its Ag (I) complex. These studies show that:

-structural classification of sulfonated azo dye salts as solvent-separated ion-pair, as simple complexes, or as higher-connectivity complexes can be extended to s-block salts of Orange G.

- the nature of the metal ion guides the structural type adopted, with the more electronegative metals favoring M-OH$_2$ bond formation and hence solvent separated ion-pairs, and the more electropositive metals forming higher-connectivity complexes with more M-O$_3$S bond formation.

- Orange G is a poorer ligand for s-block metals than *para* - or *meta*- monosulfonated azo dyes.

- the sodium salt of Orange G forms a 3-dimensional coordination polymer, with both the sulfonate and the keto oxygen atom involved in metal bonding.

- in the solid state Orange G exists largely as ketohydrazone tautomer with an intramolecular hydrogen bond between the keto and hyrazo forms.

In coordination polymer self-assembly free metal ions are commonly used as building blocks, and macrocyclic complexes have seldom been employed [14,15]. However, macrocyclic complexes offer an advantage. Free metal ions contain many binding sites and the direction of network extension cannot be easily controlled. Square-planar macrocyclic complexes contain only two empty *trans* coordination sites and act as a linear linker for the ligand. These complexes enable control of the extension direction and simplify the structure [14,15].

Only a few sulfonated coordination polymers containing metal-macrocyclic complexes have been reported, *i.e.,* [Cd(cyclam)(1,5-nds)]$_2$ (1,5-nds = naphthalene-1,5-disulfonate) [16,17], [Co(cyclam) (H$_2$O)$_2$] (1,5-nds)•2H$_2$O [2,18], [Cu(1,4,6,8,11–pentaaza-13-methyl-6(1-phenylethyl-cyclotetradecane) (methanedisulfonate)] [16,19], [Cu(cyclam)(1,5-nds)]$_n$ [16,20], {[Ni(cyclam)(1,5-nds)]•1/3(H$_2$O)}$_n$ [17,19], [Ni(cyclam)(1,5-nds)]$_n$•nH$_2$O [16,18], [Cu(cyclam) (PTMSO$_3$)$_2$]•6EtOH [21] and [Cu(cyclam)](PTMSO$_3$)$_2$ [21] (PTMSO$_3$ = polychlorotriphenylmethylsulfonate). The different coordination modes observed in this series Co^{2+}/μ^0, Ni^{2+}/μ^1, Cu^{2+}/μ^1 and Cd^{2+}/μ^2 demonstrate that coordination strength increases Co^{2+} < Ni^{2+} < Cu^{2+} < Cd^{2+} [2].

Coordination polymers of sulfonated azo dyes with metal macrocyclic complexes have not been reported. Considering the advantages offered by metal-macrocyclic complexes and the ability of azo dyes to coordinate electropositive metals, we prepared these polymers using the sulfonated azo dye ligand 4-hydroxy-3-(4-sulfonato-1-naphthylazo)naphthalen-1-sulfonate (carmoisine) and Cu^{II} and Ni^{II} complexed by 1,4,8,11-tetraazacyclotetradecane (cyclam).

2. Experimental Procedure

2.1. General

All chemicals were reagent grade obtained from commercial sources and used without further purification. Distilled water was used for all procedures. FTIR spectra of solid samples were recorded on a JASCO 610 instrument in KBr pellets or Nujol.

Backscattered powder Raman spectra were recorded at room temperature with a JASCO NRS 3300 spectrophotometer equipped with a CCD detector (-69^{0}C) using a 600 L mm^{-1} grating with spectral resolution 0.65 cm^{-1}. Calibration was based on the Si 521 cm^{-1} peak. Excitation was 100 mW at 758 nm. The incident laser beam (1 µm diameter at the sample surface) was focused through an Olympus microscope.

Thermogravimetric analyses (TGA) were performed in air (100 mL min^{-1}) on a TA STD Q 600 instrument from 25-750^{0}C at 5^{0}C min^{-1}.

Powder XRD patterns were obtained with a Bruker D8 Advance powder diffractometer at 40 kV and 40 mA, equipped with an incident beam Ge 111 monochromator using CuKα$_1$ radiation (λ = 1.540598 Å). The patterns were indexed using the Dicvol method [22].

Elemental analyses were performed with a THERMO FINNIGAN EA 1112H T O/H-N/C, instrument. UV spectra were recorded on a Unicam UV4 spectrophotometer (MgO as standard).

2.2. Preparation of {[Cu^{II}(cyclam)](carmoisine dianion) (H$_2$O)$_5$}$_n$ (4) and {[Ni^{II}(cyclam)] (carmoisine dianion)}$_n$ (5)

[Cu^{II} (cyclam)] (ClO$_4$)$_2$ (**2**) and [Ni^{II} (cyclam)] (ClO$_4$)$_2$ (**3**) were prepared according to the published procedures [23,24].

Caution: The perchlorate salts are potentially explosive and should be handled in small quantities.

2.2.1. Preparation of {[Cu^{II}(cyclam)](carmoisine dianion)(H$_2$O)$_5$}$_n$ (4)

To a DMF (10 mL) solution of [Cu^{II}(cyclam)] (ClO$_4$)$_2$ (0.260 g, 0.5 mmol) an aqueous solution (5 mL) of 4-hydroxy-3-(4-sulfonato-1-naphthylazo) naphthalen-1-sulfonate disodium salt (carmoisine) (0.251 g, 0.5 mmol) was added dropwise. The solution was allowed to stand at room temperature for a week. The resulting red precipitate (0.150 g) was filtered, washed by sonication with methanol until the wash was colorless, and dried at room temperature. The precipitate is insoluble in organic solvents and has a low solubility in water. Analysis: Calc. for C$_{30}$H$_{46}$N$_6$O$_{12}$S$_2$Cu: C, 44.46; H, 5.72; N, 10.37. Found: C, 44.58; H, 5.80; N, 10.25. IR (KBr, cm^{-1}): 3280 ms, 3169ms, 2928ms, 2870ms, 1604w, 1577w, 1499s, 1474ms, 1432ms, 1366s, 1335w, 1276ms, 1222s, 1182s, 1130w, 1099w, 1039 vs, 1018vs, 1001s, 888w, 810vw, 757 bw, 727vw, 686s, 652ms, 638w, 625s, 595w, 554w, 536w, 500vw, 467vw, 433vw. Raman (powder, cm^{-1}): 1569s, 1512ms, 1437s, 1403w, 1360s, 1335w, 1278vs, 1232s, 1160w, 1115w, 1046w, 1001ms, 954vw, 729w, 679ms, 651w, 553w, 531ms, 501ms, 467s, 423w, 369w, 274ms, 225vw, 193vw, 136vw, 54 s.

2.2.2. Synthesis of {[Ni^{II}(cyclam)](carmoisine dianion)}$_n$ (5)

To a DMF (10 mL) solution of [Ni^{II}(cyclam)] (ClO$_4$)$_2$ (0.240 g, 0.5 mmol) an aqueous solution (5 mL) of 4-hydroxy-3-(4-sulfonato-1-naphthylazo)naphthalen-1-

sulfonate disodium salt (carmoisine) (0.251 g, 0.5 mmol) was added dropwise. The solution was allowed to stand at room temperature for two months. The resulting brown reddish precipitate (0.140 g) was filtered, washed by sonication with water until the wash solution was colorless, and dried at 100^0C. The precipitate is insoluble in organic solvents and in water. *Analysis*: Calc. for $C_{30}H_{36}N_6O_7S_2Ni$: C, 50.36; H, 5.07; N, 11.75. Found: C, 50.44; H, 5.12; N, 11.67.(1). IR (KBr, cm^{-1}): 3265ms, 3224ms, 2926ms, 2862ms, 1604w, 1575w, 1498s, 1473ms, 1433 w, 1367w, 1336vw, 1277s, 1228s, 1198s, 1167s, 1130w, 1105w, 1041vs, 1014vs, 964vw, 947w, 876w, 837vw, 762w, 723vw, 687s, 652ms, 625s, 594w, 555w, 542vw, 501vw, 469vw, 419vw. Raman (powder, cm^{-1}): 1571s, 1513s, 1447s, 1366s, 1281vs, 1230ms, 1117vw, 1051w, 1006w, 952,vw 731w, 680ms, 535ms, 504ms, 472ms, 424w, 382w, 277w, 148vw, 56 s.

3. Results and Discussion

3.1. Synthesis

Reaction of [Cu^{II}(cyclam)](ClO$_4$)$_2$ (**2**) or [Ni^{II}(cyclam)](ClO$_4$)$_2$ (**3**) in DMF with aqueous 4-hydroxy-3-(4-sulfonato-1-naphthylazo)naphthalen-1-sulfonate disodium salt (carmoisine) (**1**) formed coordination polymers {[Cu^{II}(cyclam)](carmoisine dianion)(H$_2$O)$_5$}$_n$ (**4**) and {[Ni^{II}(cyclam)](carmoisine dianion)}$_n$ (**5**), respectively (Scheme 1).

The coordination polymers **4** and **5** consist of one-dimensional chains resulting from coordination of cyclam complexed metals by the SO$_3$ groups of carmoisine, in agreement with IR and Raman spectra, DSC-TGA, and elemental analysis. In [Cu(1,4,6,8,11–pentaaza-13-methyl-6-(1-phenylethyl-cyclotetradecane) (methanedisulfonate)] [17,20], [Cu(cyclam)(1,5-nds)]$_n$ [16,20] and in [Ni(cyclam)(1,5-nds)]$_n$•nH$_2$O [16,18] each SO$_3$ group coordinates monodentately to Cu^{2+} or to Ni^{2+} and forms two hydrogen bonds with cyclam NH groups. This coordination mode is probable in compounds **4** and **5**. The carmoisine ions behave as bifunctional spacers,

linking the complex cations into infinite 1 D strings (Scheme 2: hydrogens other than those in hydrogen bonding are omitted and the molecule was geometrically optimized using the B3PW91/LANL2DZ basis set).

The UV spectrum of solid polymer **4** shows the characteristic features of Ni^{2+} (d^8) ion in a distorted octahedral environment: two bands at 410 nm and 720 nm correponding to the $^3A_{2g}$ (F)$\rightarrow$ $^3T_{1g}$(F) (υ_2) and $^3A_{2g}$ (F)$\rightarrow$ $^3T_{1g}$(P) (υ_3) transitions. The reflectance spectrum of polymer **5** presents a broad absorption centered at aproximately 715 nm suggesting a distorted octahedral environment around the Cu(II) d^9 ion. This band can be attributed to the $^2E \rightarrow ^2A_1$ transition. Three transitions are expected (d$_{xy}$, d$_{yz} \rightarrow$d$_x{}^2$ and d$_{xy} \rightarrow$ d$_{x-y}{}^2$) but these are very close in energy and give rise to a single broad band.

3.2. Powder X-ray diffraction

Growth of single crystals of compounds **4** and **5** failed, so they were characterized by powder XRD (Figs. 1 and 2).
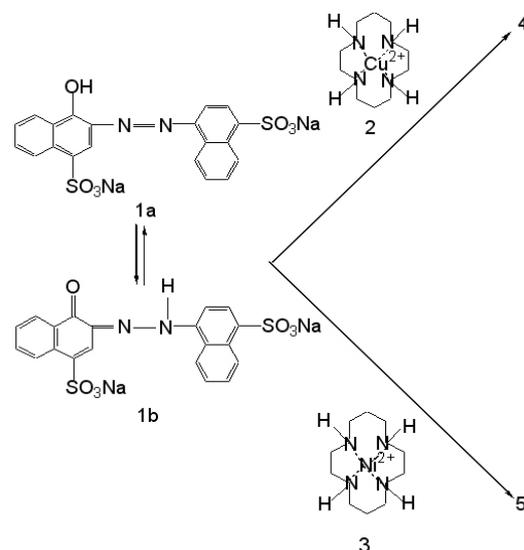
Scheme 1. Formation of polymers **4** and **5**.
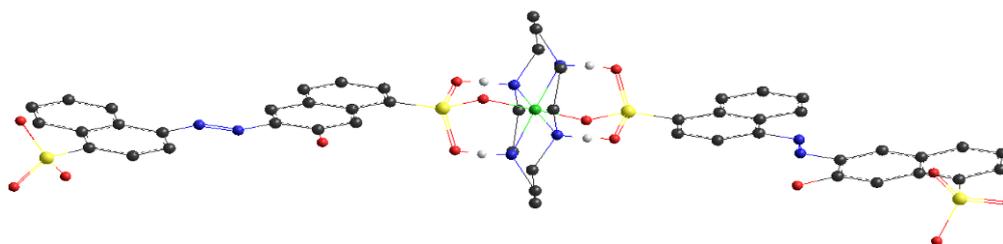
C= black, O= red, S= yellow, N= blue, Me^{2+} (Cu^{2+}, Ni^{2+}) = green , H=white

Scheme 2. Geometrically optimized molecules of **4** and **5**.
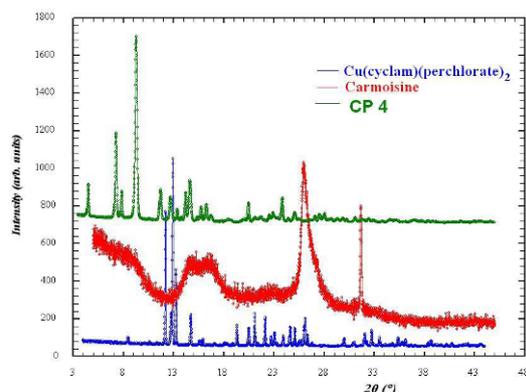
Figure 1. PXRD patterns for {[Cu^{II}(cyclam)](carmoisine dianion) (H$_2$O)$_5$}$_n$ (**4**) and for starting materials.
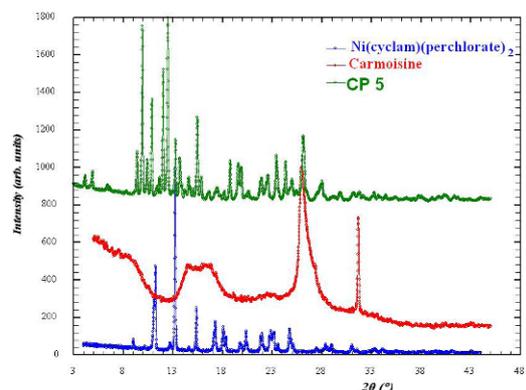
Figure 2. PXRD patterns for {[Ni^{II}(cyclam)](carmoisine dianion)}$_n$ (**5**) and for starting materials.

Figure 3. DSC-TGA curves for {[Cu^{II}(cyclam)](carmoisine dianion) (H$_2$O)$_5$}$_n$ (**4**).
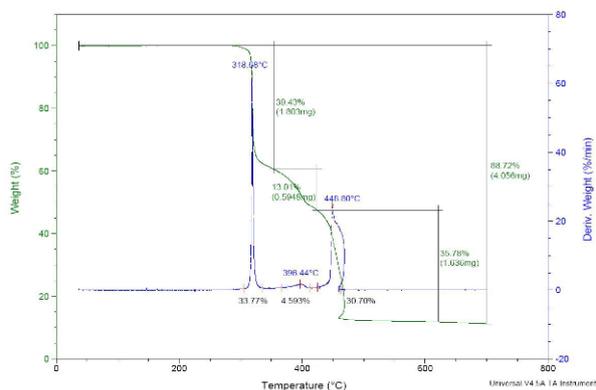
Figure 4. DSC-TGA curves for{[Ni^{II}(cyclam)](carmoisine dianion)}$_n$ (**5**).

The PXRD patterns of compounds **4** and **5** are completely different from those of the starting materials, demonstrating the formation of coordination polymers. Crystallographic data are shown in Table 1.

3.3. Thermal gravimetric analysis

Thermal gravimetric analyses of compounds **4** and **5** are shown in Figs. 3 and 4.

Thermogravimetric analysis (TGA) of **4** shows a first weight loss of 10.91% at 20-70⁰C, corresponding to the loss of five water molecules per formula unit. Differential scanning calorimetry (DSC) indicates that **4** loses these water molecules at 25-70⁰C, centered at 53.19⁰C, the host being stable up to 300.46⁰C. On further heating, three consecutive weight losses were observed 300.46-416.65⁰C with the loss of carmoisine dianion and macrocyclic ligand. Finally, the CuO residue (observed 9.02%, calculated 9.83%) remained above 416.65⁰C. The guest water molecules can be eliminated by heating at 100⁰C without modification of the PXRD patterns.
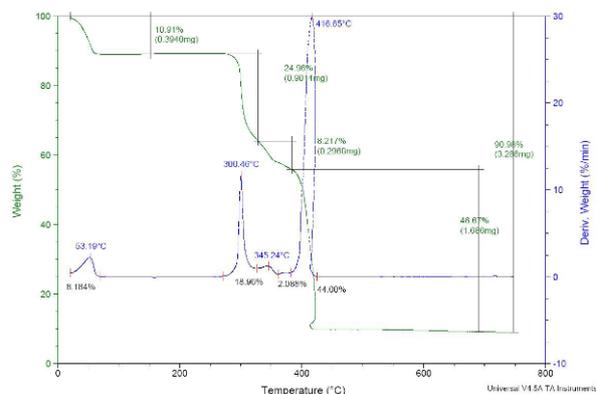
TGA of **5** indicates that no solvent is present in the crystal structure. DSC shows that the host is stable up to 326.68⁰C, and then three consecutive weight losses take place over 318.68-448.80⁰C, corresponding to azo dye and macrocyclic ligand decomposition. The NiO residue (observed 11.28%, calculated 10.43%) remained above 448.80⁰C.

3.4. Vibrational spectra analyses

The infrared and Raman spectra are depicted in Figs. 5 and 6.

3.4.1. Cyclam vibrations

The infrared spectra display two medium strong N-H stretching bands at 3169 cm^{-1} and 3280 cm^{-1} (**4**), and at 3265 cm^{-1} and 3224 cm^{-1} (**5**); two medium strong asymmetric and symmetric CH$_2$ stretching bands at 2928 cm^{-1} and 2870 cm^{-1} (**4**), and at 2926 cm^{-1} and 2862 cm^{-1} (**5**); and a medium strong deformation band at 1474 cm^{-1} (**4**) and 1473 cm^{-1} (**5**) [25].

3.4.2. Hydroxyl vibrations

The presence of an OH group *ortho* to azo provides an extra hydrogen bonding site in similar compounds. In the IR spectrum of carmoisine the broad intense band at 3436 cm^{-1} is attributed to hydrogen bonded OH vibration [26]. In compounds **4** and **5** broad intense bands appear at 3446 and 3435 cm^{-1}, respectively (Nujol).
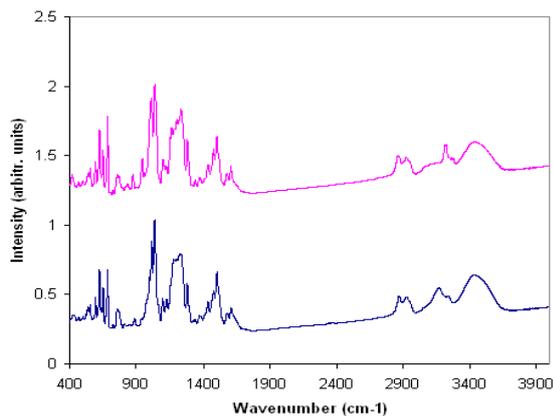

Figure 5. Experimental infrared spectra recorded in solid state of $\{[Cu^{II}(cyclam)](carmoisine\ dianion)\ (H_2O)_5\}_n$ (**4**) (down) and $\{[Ni^{II}(cyclam)](carmoisine\ dianion)\}_n$ (**5**) (up).
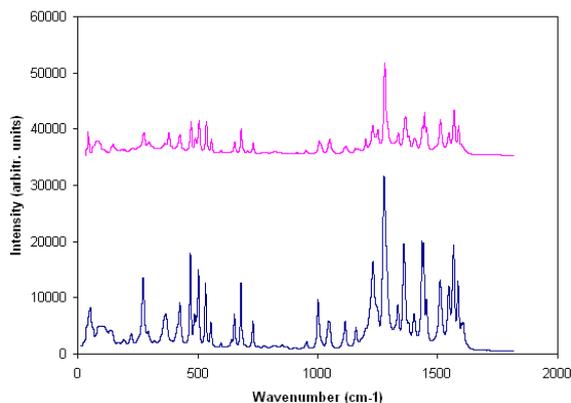

Figure 6. Experimental Raman spectra recorded in solid state of $\{[Cu^{II}(cyclam)](carmoisine\ dianion)(H_2O)_5\}_n$ (**4**) (down) and $\{[Ni^{II}(cyclam)](carmoisine\ dianion)\}_n$ (**5**) (up).

The in-plane OH bending appears as a strong band at 1499 cm^{-1} (**4**) and 1498 cm^{-1} (**5**) [26]. The OH out-of plane deformation lies in the region 280-312 cm^{-1} for free OH and 600-720 cm^{-1} for associated OH [27]. The strong band at 652 cm^{-1} (**4** and **5**) and medium intense band at 652 cm^{-1} (**4**) and 653 cm^{-1} (**5**) in the Raman spectra are due to hydroxyl out-of plane bending [26].

3.4.3. Azo chromophore (-C-N=N=C-) vibrations

Due to symmetry, N=N stretching has a very characteristic and intense Raman band but is difficult to observe in the IR. When just one naphthalene ring is OH-substituted a change in N=N bond length produces a change in dipole moment, making the mode IR-active with medium intensity. The band between 1450 cm^{-1} and 1380 cm^{-1} corresponds to an azo stretch [28]. Azo C-N stretching appears in the 1200-1130 cm^{-1} region (IR) [29,30]. Substituents on conjugated naphthalene groups influence both the peak wave number and intensity [26]. The intense band observed at 1360 cm^{-1} for **4** and 1366 cm^{-1} for **5** in the Raman spectrum and the weak bands at 1366 cm^{-1} for **4** and 1367 cm^{-1} for **5** in the IR spectrum can be attributed to the azo stretch.

This large shift can be explained by greater conjugation and π-electron delocalization [31]. Theoretical calculation [26] showed that the azo bond length is 128.8 pm in carmoisine. The calculated N=N bond distance is 124.5-125.0 pm for the OH tautomer but the N-N bond in the NH tautomer is 130.0 pm [32]. The *ortho* OH-substituted naphthalene ring in carmoisine has an average C-C bond of 140.9 pm, which is between a C-C (154 pm) and a C=C (134 pm). The calculated average C-N (141.4 pm) is also intermediate between C-N (148 pm) and C=N (128 pm) [26]. These calculations show π-electron delocalization over the naphthyl azo system, which is responsible for the molecule's nonlinearity [33].

In comparison the azo distance in carmoisine is appreciably elongated. This can be explained by

Table 1. Crystal data for coordination polymers **4** and **5**.

Compounds	Elementary lattice		Crystal system	Space group	Z	Volume Å³	ρ calc. g cm⁻³	ρ det.** g cm⁻³
	Å	Degree						
4	a = 19.613 b = 12.242 c = 18.419	α = 88.766 β = 93.669 γ = 101.194	triclinic	P₋₁	2	1977	1.215	1.200
5	a = 21.357 b = 18.226 c = 8.213	α = 83.305 β = 90.660 γ = 93.623	triclinic	P₋₁	2*	3160	1.500	1.380

*Asymmetric unit consists of 2 molecules
**Density was determined by picnometer method

hydroxyl group donation of electron density into the azo π^* orbital via the naphthalene ring. Decreased azo bond order and bond lengthening take place, indicating the presence of the NH tautomer **1b** in the solid.

The IR and Raman spectra support the presence of the NH form in polymers **4** and **5,** based on the recent paper of Oliveira *et al.* [32a]. Their calculated IR spectra show similar band profiles for the NH and OH tautomers of trisodium 2-hydroxy-1-(4-sulfonato-1-naphtylazo) naphthalene-6,8-disulfonate (azo dye E124), with the main differences in the 1600 and 1200 cm^{-1} region. For the NH isomer, intense bands are predicted at 1554 (assigned to a combination of δNH, νCO, ν C=N, and βCH), 1324 and 1294 cm^{-1}(attributed to δNH, νN-H, βCH, and νCC). All of these are characteristic of the NH isomer and may be used as fingerprints.

Experimentally, corresponding absorptions are observed at 1495, and 1221 cm^{-1} in azo dye E124. In the Raman spectrum, which is more sensitive to the tautomeric forms than the IR, three bands were observed around 1574,1515 and 1364 cm^{-1}, assigned to δNH, νC=O + νC=N, and νCC. These bands are predicted only for the NH species at 1606, 1554 and 1375 cm^{-1}. For polymer **4** the corresponding bands of the NH tautomer appear at 1499 and 1222 cm^{-1}(IR) and at 1569, 1512 and 1360 cm^{-1} (Raman). For polymer **5** these bands appear at 1498 and 1367 cm^{-1} (IR) and at 1571, 1513 and 1366 cm^{-1} (Raman). These are mixed with other vibrations, especially with naphthalene ring stretching modes or OH in-plane-bending, as noted above.

The intense IR bands at 1276 cm^{-1} for **4** and 1277 cm^{-1} for **5** as well as at 1278 cm^{-1} for **4** and 1280 cm^{-1} for **5** in the Raman originate from stretching of C-N connected to a naphthalene ring lacking OH, plus a second contribution from C-H in-plane bending of the same ring [25]. The weak Raman band at 1160 cm^{-1} (**4**) and 1162 cm^{-1} (**5**) is due to stretching of the C-N group connected to the OH-substituted naphthalene ring [26]. The strong band in the Raman at 1232 cm^{-1} (**4**) and 1230 cm^{-1} (**5**) can be assigned to asymmetric (C-N=N-C) stretching combined with the C-O stretch [24]. The intense band at 1018 cm^{-1} (**4**) and 1014 cm^{-1} (**5**) in the IR and weak bands at 1001 cm^{-1} and 1006 cm^{-1} in the Raman are attributed to (C-N=N-C) in-plane-bending. The intense IR band at 625 cm^{-1} (both **4** and **5**) is assigned to (C-N=N-C) and naphthalene in-plane-bending [26].

3.4.4. Sulfonate group vibrations

Asymmetric SO$_3$ vibrations in sulfonic acid salts usually occur in the IR at 1250-1140 cm^{-1} [25]. The symmetric stretch is sharper and occurs at 1130-1080 cm^{-1}. SO$_3$

symmetric deformation modes give strong bands in the 550-660 cm^{-1} region (IR) [34,35].

The sulfonate group does not affect the conjugated system irrespective of its position on the naphthalene ring. Changes in electron density are relatively low at the carbon atom bound to the sulfonate [36]. Participation of sulfur d orbitals in the conjugated system is very low, and the π contribution to C-S bonding is practically negligible [26].

The asymmetric stretching mode of SO$_3$ is mixed with C-N stretching and C-H in-plane bending [26] giving very broad IR bands at 1182 cm^{-1} (**4**) and 1198 cm^{-1} (**5**). The very intense IR band at 1039 cm^{-1} (**4**) and 1041 cm^{-1} (**5**) and medium intense Raman band at 1046 cm^{-1} (**4**) and 1051 cm^{-1} (**5**) can be attributed to SO$_3$ symmetric stretching mixed with naphthalene ring deformations [26]. SO$_3$ symmetric bending is coupled with out-of-plane bending or with naphthalene ring deformations giving broad IR bands at 757 cm^{-1} (**4**) and 761 cm^{-1} (**5**) and an intense band at 686 cm^{-1} (**4**) and 687 cm^{-1} (**5**).

The medium intensity Raman bands at 501 cm^{-1}, 467 cm^{-1} (**4**) and 504 cm^{-1}, 472 cm^{-1} (**5**) correspond to SO$_3$ wagging. The same mode appears at 500 cm^{-1}, 467 cm^{-1} (**4**) and 501 cm^{-1}, 469 cm^{-1} (**5**) in the IR spectra. Weak bands at 369 cm^{-1}, 300 cm^{-1} (**4**) and 382 cm^{-1}, 305 cm^{-1} (**5**) in the Raman are assigned to SO$_3$ rocking mixed with torsion vibrations of the naphthalene rings and the azo group [26].The strong Raman band at 54 cm^{-1} for **4** and 56 cm^{-1} for **5** belongs to torsions of the SO$_3$ group and naphthalene rings.

3.4.5. Naphthalene ring vibrations

Naphthalene ring vibrations make major contributions in the IR and Raman spectra. Ring stretching is expected in the region 1620-1390 cm^{-1} while naphthalene CH bending occurs at 1230-970 cm^{-1} [37a,37b]. These vibrations are mixed with OH in–plane bending, and coupled to C-N stretching or to SO$_3$ vibrations.

4. Conclusion

Two new polymers were prepared by coordination of [Cu^{II}(cyclam)](ClO$_4$)$_2$ (**2**) or [Ni^{II}(cyclam)](ClO$_4$)$_2$ (**3**) with carmoisine (**1**). Single-crystal growth failed so their crystalline properties were characterized by powder XRD. The polymer structures proposed were also supported by IR and Raman spectra, DSC-TGA, and elemental analysis.

One of the differences between small model dyes and the larger, more complex colorants consists in the latter's adoption of the keto-hydrazone form rather than the simple azo form [10]. The sulfonic group

does not affect the conjugated system irrespective of its position on the naphthalene ring, and changes in the electron density are relatively low at the carbon atoms to which sulfonate is bonded. Due to this lack of interaction between the sulfonate group and the naphthalene ring the coordination of Cu[II] or Ni[II] cyclam complexes by carmoisine does not influence the π electron delocalization in their coordination polymers. The presence of both NH and OH tautomers in the solid is shown by their IR and Raman spectra.

Acknowledgements

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