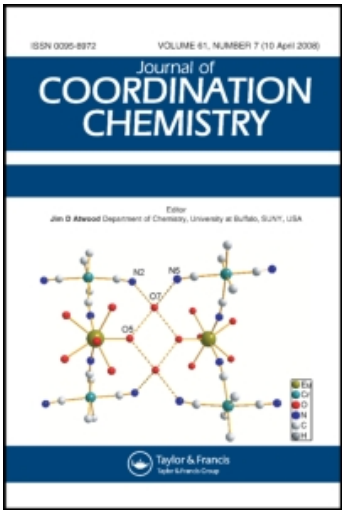

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Synthesis, characterization, critical micelle concentration determination, and antimicrobial studies of some complexes of chromium(III) metallosurfactants

Narayanasamy Kumaraguru[a]; Kannappan Santhakumar[b]
[a] School of Chemistry, Bharathidasan University, Tiruchirappalli, Tamil Nadu, India [b] Chemistry Division, School of Science and Humanities, Vellore Institute of Technology, VIT University, Vellore, Tamil Nadu, India

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Synthesis, characterization, critical micelle concentration determination, and antimicrobial studies of some complexes of chromium(III) metallosurfactants

NARAYANASAMY KUMARAGURU† and KANNAPPAN SANTHAKUMAR*‡

†School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, Tamil Nadu, India
‡Chemistry Division, School of Science and Humanities, Vellore Institute of Technology, VIT University, Vellore 632 014, Tamil Nadu, India

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Surface active mixed-ligand complexes of Cr(III) containing chelating ligands, namely ethylenediamine (en), triethylenetetramine (trien), 2,2-bipyridine (bpy), and 1,10-phenanthroline (phen) with different axial amine ligands (dodecylamine or cetylamine) were synthesized and characterized by UV–Vis, infrared, and NMR spectroscopies and elemental analysis. The magnetic moments (3.6–3.8 B.M.) are close to the spin-only value for a d^3 Cr(III) in octahedral symmetry. The critical micelle concentration values of these surfactant metal complexes in aqueous solution were determined as a function of temperature using conductometric technique. Thermodynamics of micellization (ΔG^0_m, ΔH^0_m and ΔS^0_m) were evaluated. Dodecyl/cetylamine metallosurfactants obtained were tested for antibacterial and antifungal activities having good activities.

Keywords: Synthesis; Chromium(III); CMC; Micelles; Mixed-ligand complexes

1. Introduction

Chromium is an essential nutrient for proper carbohydrate and lipid metabolism in mammals. We are interested in the synthesis and micelle forming properties of metal complexes containing lipophilic ligands [1–4]. As in biology, such compounds may exhibit physical and chemical properties with interesting and useful applications. The expanding ability to mimic form and structure in biology has largely been achieved using the self-assembly of well-defined and complex molecular entities from constituent subunits in solution. Unlike biology, however, self-assembly in coordination chemistry occurs through the formation of coordinate bonds rather than weak inter- or intramolecular interactions. Self-assembly in coordination chemistry consequently provides

*Corresponding author. Email: lovingsantha@gmail.com

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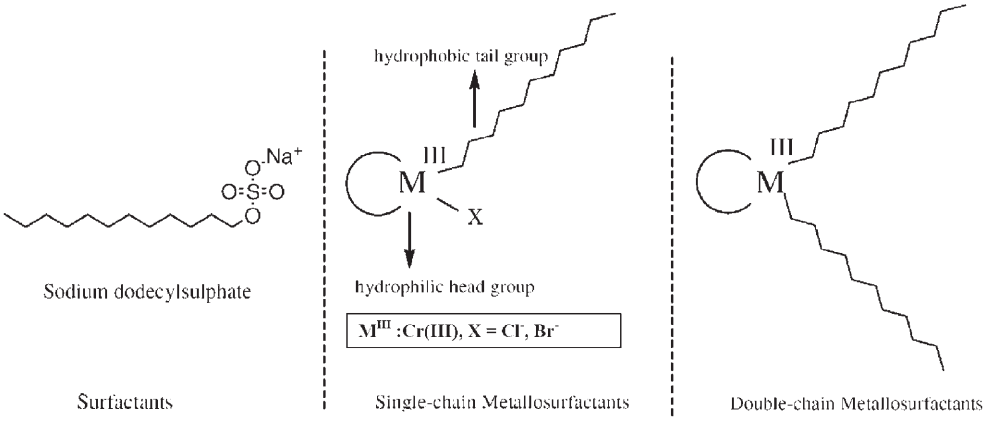
an important and powerful entry into supramolecular engineering and the associated fields of solid-state and crystal engineering [5, 6].

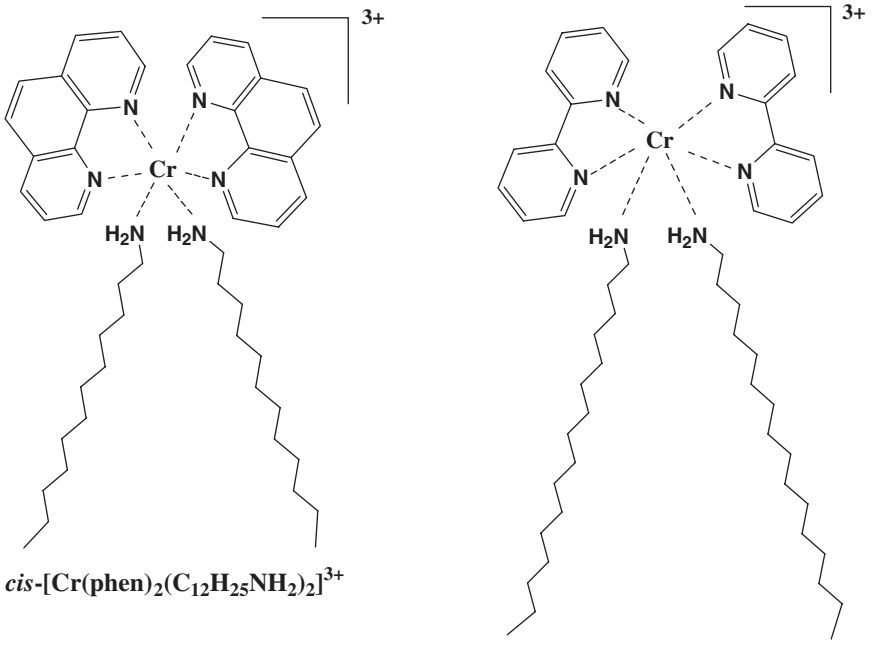
A characteristic feature of transition metals is their ability to form complexes with ligands such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). The photophysics and photochemistry of complexes of these ligands are under active investigation with particular interest in their application to solar energy conversion schemes. A common feature of these ligands is the presence of a vacant π orbital that can accept electron density from the metal ion to form a type of π bonding that supplements the σ bonding arising from the donation of lone pair electrons. Most metal complexes containing bpy and phen chelators can act as potential anti-tumor agents.

Metallosurfactants have received a sustained level of attention [7–12] due to their relevance in various redox processes in the biological system and are promising agents as anthelmintics [13], antiparasitics [14], antibiotics [15], and because of their multiple applications in fields such as medicine [16], magnetic resonance imaging [17] and drug delivery [18]. Metallosurfactants with chelating ligands are of interest for metallobiomolecules in the search for appropriate systems for binding and activating simple molecules, catalysis, and magnetic interactions [8, 19]. Surfactant–metal complexes are a special type of surfactants, where a coordination complex acts as the surfactant (schemes 1 and 2). In these surfactants, the metal complex containing the central metal ion with its primary coordination sphere acting as the head group and the hydrophobic part of one or more ligands acts as the tail. Like other well-known surfactants, these metallosurfactants also form micelles at a specific concentration called critical micelle concentration (CMC) in aqueous solution.

Because of great effort and success in the study of metallosurfactants of chromium(III) complexes, such complexes have attracted much attention due to their interesting properties and the relative simplicity of their synthesis. As a part of our study on transition metal-based surfactants [1–4, 20, 21], in this article we report the synthesis, characterization, and determination of CMC values of Cr(III) metallosurfactants.



Scheme 1. Structure of surfactants and metallosurfactants.



Scheme 2. 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) chromium(III) complexes.

2. Experimental

2.1. *Materials*

Reagents were of analytical grade (Aldrich and Merck). Ultra pure water, obtained by deionizing distilled water (conductivity $< 10^{-6}\,S\,m^{-1}$) using a Milli-Q Reagent Grade water system, was used for preparative work and to make up solutions for all physical measurements.

2.2. *Physical measurements and methods*

Electronic absorption spectra were taken in 10^{-3} M perchloric acid medium recorded in a Varian Cary 500 Scan UV–Vis-NIR spectrophotometer. Infrared (IR) spectra were recorded on a Jasco 460 plus spectrometer using KBr discs. ^{1}H NMR spectra were recorded in deuterated solvents using a Bruker AC 300F (300 MHz) spectrometer with TMS as internal reference. C, H, and N were estimated using a Perkin-Elmer 2400 CHN instrument. Conductance measurements were carried out in aqueous solutions of complexes with a Metrohm 712 conductivity meter and a dip-type cell with a cell constant of 1.0.

2.3. *Synthesis of single-chain metallosurfactants of chromium(III) complexes*

2.3.1. *cis*-[Cr(bpy)$_2$($C_{12}H_{25}NH_2$)Cl](ClO$_4$)$_2$ and *cis*-[Cr(bpy)$_2$($C_{16}H_{33}NH_2$)Cl](ClO$_4$)$_2$. *cis*-[Cr(bpy)$_2$Cl$_2$]Cl (3 g) [22] was dissolved in water (10 mL). To this

solution dodecylamine (1 mL), where the amine used was not sufficiently soluble in water, was first mixed with ethanol (2 mL) and then added dropwise over a period of 30 min. The brown-red solution gradually became pale during the reaction. The mixture was set aside at 313 K for 2 days until no further change was observed, then a saturated solution of sodium perchlorate in very dilute perchloric acid was added. Slowly a pasty solid mass separated was filtered off, washed with small amounts of alcohol followed by acetone, and then dried in air. The semi-dried solid was further dried in a drying pistol over fused calcium chloride and stored in a vacuum desiccator. For *cis*-$[Cr(bpy)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$, cetylamine was used in place of dodecylamine.

2.3.2. *cis*-$[Cr(bpy)_2(C_{12}H_{25}NH_2)Br](ClO_4)_2 \cdot 2H_2O$ and *cis*-$[Cr(bpy)_2(C_{16}H_{33}NH_2)Br](ClO_4)_2 \cdot 2H_2O$. These complexes were synthesized by the same method as described for *cis*-$[Cr(bpy)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2 \cdot 2H_2O$ except that in place of *cis*-$[Cr(bpy)_2Cl_2]Cl$, *cis*-$[Cr(bpy)_2Br_2]Br$ [23] was used.

2.3.3. *cis*-$[Cr(phen)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$, *cis*-$[Cr(phen)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$, *cis*-$[Cr(phen)_2(C_{12}H_{25}NH_2)Br](ClO_4)_2$, and *cis*-$[Cr(phen)_2(C_{16}H_{33}NH_2)Br](ClO_4)_2$. The procedure for synthesizing these complexes is similar to that described above, but in place of bipyridine, phenanthroline complexes *cis*-$[Cr(phen)_2Cl_2]Cl$ and *cis*-$[Cr(phen)_2Br_2]Br$ were used [24].

2.4. *Synthesis of double-chain metallosurfactants of chromium(III) complexes*

2.4.1. *cis*-$[Cr(en)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ and *cis*-$[Cr(en)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$. *cis*-$[Cr(en)_2Cl_2]Cl$ [25] (3.0 g) was dissolved in water (20 mL). To this solution, slightly more than the calculated amount of dodecylamine (4.3 mL) in ethanol (3 mL) was added dropwise over a period of 30 min. The purple solution gradually became lighter and the mixture was set aside for 2 days at 313 K. Afterwards a saturated solution of sodium perchlorate in very dilute perchloric acid was added, the solid was filtered off, washed with alcohol followed by acetone and dried.

The complexes *cis*-$[Cr(en)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$, *cis*-$\alpha$-$[Cr(trien)(C_{12}H_{25}NH_2)_2](ClO_4)_3$, *cis*-$\alpha$-$[Cr(trien)(C_{16}H_{33}NH_2)_2](ClO_4)_3$, *cis*-$[Cr(bpy)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$, *cis*-$[Cr(bpy)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$, *cis*-$[Cr(phen)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$, and *cis*-$[Cr(phen)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$ were prepared by the ligand substitution method by replacing the chloride ion with dodecylamine/cetylamine from their corresponding parent complexes [22–26].

Caution: Perchlorate salts of surfactant–Cr(III) complexes containing organic ligands are potentially explosive! Although we have experienced no problems with the compounds reported in this work, they should only be handled in small quantities and never scraped from sintered glass frits, nor heated in the solid state.

2.5. *Determination of CMC*

The CMC values of the complexes were calculated using electrical conductance data measured using a digital conductivity meter (Metrohm 712). The conductivity cell

(dip-type with cell constant of 1.0) was calibrated with KCl solutions in the appropriate concentration range. The cell constant was calculated using molar conductivity data for KCl published by Barthel *et al.* [27]. Various concentrations of surfactant–Cr(III) complexes were prepared in the range of 10^{-6}–10^{-2} mol dm^{-3}. All measurements were performed in a double-walled glass container, which was maintained at the desired temperature (±0.1 K) using a circulating water bath. The conductivities of these solutions were measured at 303–313 K. Conductance was measured after thorough mixing and temperature equilibrating at each dilution. The measurement started with a dilute solution and subsequent concentrated solutions were prepared by adding a previously prepared stock solution. The establishment of equilibrium was checked by taking a series of readings after 15 min intervals until no significant change occurred.

2.6. *Microbial assay*

The complexes have been tested *in vitro* to evaluate their antimicrobial screening for its effect on certain bacteria and fungi by the disc diffusion method [28]. The complex was stored at room temperature and dissolved in DMSO. Bacterial organisms used in the present investigation were isolated from human beings with characteristic infections and diseases. The isolates were pathogenic. The pathogens used included both gram positive and gram negative (*Escherichia coli*, *Staphylococcus aureus*, *Proteus vulgaris*, and *Bacillus subtilis*) bacteria were grown in nutrient agar medium and incubated at 35°C for 48 h followed by frequent subculture to fresh medium and were used as test bacteria. Fungi were incubated at 30°C for 72 h followed by periodic subculturing to fresh medium. Petriplates were inoculated with a loop full of bacterial and fungal culture and spread throughout the petriplates uniformly with a sterile glass spreader. To each disc the test samples (10 ppm) and reference ciprofloxacin (1 μg per disc for bacteria) and clotrimazole (10 μg per disc for fungi) were added with a sterile micropipette. Plates containing the respective solvents served as control. Inhibition was recorded by measuring the diameter of the inhibitory zone after incubation. Triplicates were maintained and the experiment was repeated thrice and the average values are presented.

3. Results and discussion

Surfactant–chromium(III) complexes synthesized in the present study were characterized by UV–Vis, IR, and NMR spectra, checked by comparing spectra with those for the corresponding complexes where one ligand is butylamine instead of dodecylamine/cetylamine reported earlier [29]. The purity of the complexes was checked by elemental analyses [30], which were in good agreement with calculated values (table 1).

3.1. *Spectroscopic characterization*

3.1.1. Electronic absorption spectra. The wavelength of the first absorption maximum in aqueous perchlorate medium for each complex is given in table 1. Absorption spectra [31, 32] of the *cis* and *trans* forms of $[M(en)_2(NH_3)Y]^{n+}$ (Y = Cl or H_2O) show some

Table 1. Microanalysis and visible spectra of some chromium(III) metallosurfactants.

Surfactants	λ_{max} (nm)	μ_{eff} (B.M.)	Yield (%)	% Found (calculated)				
				Cr	C	H	N	Cl/Br
cis-$[Cr(en)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	510	3.72	56	6.1 (6.2)	39.6 (40.0)	7.4 (7.7)	9.8 (10.0)	–
cis-$[Cr(en)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$	492	3.64	62	5.2 (5.4)	45.1 (45.3)	8.2 (8.4)	8.6 (8.8)	–
cis-α-$[Cr(trien)(C_{12}H_{25}NH_2)_2](ClO_4)_3$	473	3.70	58	6.2 (6.0)	44.0 (44.3)	7.8 (7.9)	9.9 (9.7)	–
cis-α-$[Cr(trien)(C_{16}H_{33}NH_2)_2](ClO_4)_3$	470	3.81	60	5.3 (5.3)	49.3 (49.0)	8.8 (8.6)	8.5 (8.5)	–
cis-$[Cr(bpy)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$	521	3.75	63	6.4 (6.6)	48.8 (49.0)	5.1 (5.4)	8.8 (8.9)	4.6 (4.5)
cis-$[Cr(bpy)_2(C_{12}H_{25}NH_2)Br](ClO_4)_2$	525	3.64	66	6.1 (6.3)	46.2 (46.4)	4.9 (5.1)	8.3 (8.4)	9.5 (9.6)
cis-$[Cr(bpy)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	507	3.83	52	4.8 (5.0)	50.7 (51.1)	6.6 (6.6)	8.0 (8.1)	–
cis-$[Cr(bpy)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$	520	3.72	61	6.1 (6.2)	51.6 (51.5)	5.9 (6.0)	8.4 (8.3)	4.0 (4.2)
cis-$[Cr(bpy)_2(C_{16}H_{33}NH_2)Br](ClO_4)_2$	526	3.71	57	5.9 (5.9)	48.4 (48.9)	5.5 (5.7)	7.8 (7.9)	9.3 (9.0)
cis-$[Cr(bpy)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$	500	3.63	50	4.2 (4.5)	54.8 (54.5)	7.6 (7.4)	7.1 (7.3)	–
cis-$[Cr(phen)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$	517	3.73	65	6.0 (6.2)	51.6 (52.0)	5.1 (5.1)	8.6 (8.4)	4.1 (4.2)
cis-$[Cr(phen)_2(C_{12}H_{25}NH_2)Br](ClO_4)_2$	522	3.82	60	5.8 (6.0)	49.2 (49.3)	4.4 (4.8)	7.7 (8.0)	8.8 (9.1)
cis-$[Cr(phen)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	508	3.71	55	4.6 (4.8)	53.3 (53.3)	6.0 (6.3)	7.6 (7.8)	–
cis-$[Cr(phen)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$	515	3.73	58	5.8 (5.9)	53.7 (54.0)	5.9 (5.7)	8.0 (7.9)	3.7 (3.9)
cis-$[Cr(phen)_2(C_{16}H_{33}NH_2)Br](ClO_4)_2$	520	3.61	65	5.5 (5.6)	51.2 (51.5)	5.3 (5.4)	7.4 (7.5)	8.2 (8.6)
cis-$[Cr(phen)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$	495	3.74	60	4.3 (4.3)	56.0 (56.3)	7.0 (7.1)	6.8 (7.0)	–

differences in the longest wavelength absorption band (d–d transition) with the *trans* form showing lower intensity ($\varepsilon < 50\,M^{-1}\,cm^{-1}$) compared to the *cis* form ($\varepsilon > 70\,M^{-1}\,cm^{-1}$). This can be used to determine the geometrical configuration of the present cations, whose longest wavelength absorption maxima are shown in table 1. The position of λ_{max} suggests that the strength of the bidentate ligands follows the order bpy < phen. Lower λ_{max} values for the complexes containing phen indicate that the basal planes are comparatively more distorted than in bpy complexes. Comparing spectra of the corresponding butylamine complexes reveal that the complexes have the same structure and the replacement of aliphatic amine by long-chain aliphatic amine ligands does not affect the symmetry of the surfactant complexes. Consequently, it does not seem that micellization greatly influences the structure of the polar head.

3.1.2. IR spectra. For the assignment of geometrical configuration to these complexes, IR spectroscopy was used. Various workers [33, 34] have employed the NH_2 deformation mode in the 1700–1500 cm^{-1} region, CH_2 rocking mode in the 900–850 cm^{-1} region, and M–N stretching mode in the 610–500 cm^{-1} region to distinguish between *cis* and *trans* isomers. Baldwin [33] suggested that the most consistent variations between spectra of *cis* and *trans* isomers were found in the CH_2 rocking region (900–850 cm^{-1}). The *cis* isomers always show two peaks, whereas *trans* isomers usually have only one. Hughes and McWhinnie [34] studied the IR absorption spectra of several *bis*(ethylenediamine) complexes and obtained a satisfactory correlation in the 610–500 cm^{-1} region, where M–N stretching modes of the chelate ring occur. No *trans* isomers had more than three strong bands, while all *cis* isomers had at least four, sometimes occurring as shoulders. The bands for the *trans* isomers were generally evenly distributed, while those for *cis* complexes occurred in two groups with a wide separation between them. Because of the lower symmetry in the present study (Supplementary material), the *cis* isomers show two bands for the NH_2 deformation, two bands for the NH_2 wagging modes, two bands for CH_2 rocking mode, and four bands as groups of two with a wide separation for the M–N stretching mode (Supplementary material). Complexes of the type *cis*-α-$[M(trien)X_2]^{n+}$ in the present study show two bands for NH_2 deformation in the region 1750–1500 cm^{-1}, two bands for the CH_2 or NH_2 twist mode in the region 1200–980 cm^{-1}, and the CH_2 rock mode in the region 945–850 cm^{-1} as two bands [35]. Strukl and Walter [36] and Schilt and Taylor [37] studied the IR spectra of several bipyridine and phenanthroline complexes, observing that the spectral shape of bpy and phen complexes were quite similar. In the spectra of phenanthroline complexes, strong bands were observed in three frequency regions between 700 and 900 cm^{-1}, between 1100 and 1250 cm^{-1}, and between 1400 and 1650 cm^{-1}. Strong bands at 700–900 cm^{-1} were attributed to the phenanthroline ring, near 725 cm^{-1} to the out-of-plane motion of hydrogens on the heterocyclic rings and the band near 830 cm^{-1} to hydrogens on the center ring. Splitting of these bands arise from out-of-plane hydrogen motion and also possibly from overtones of low-lying fundamentals.

In the spectra of bipyridine complexes, only one strong band was observed in this region as expected for two identical groups of four hydrogen atoms each. The spectra of the bpy complexes in general are less complicated than those of the phen complexes. Only three strong bands are present, one near 750 ascribed to out-of-plane bending of ring hydrogens, and one near 1450 cm^{-1} which is probably a ring frequency, and a ring

frequency near 1600 cm^{-1}. Numerous weak bands were observed between 900 and 1350 cm^{-1}. The C=C and C=N stretching vibrations of the heterocyclic ring are at 1409, 1446, 1540, and 1567 cm^{-1}. Perchlorate bands at *ca* 1100, 920, 625, and 460 cm^{-1} belong to an ionic species, not involved in coordination [38]. The IR spectroscopic data indicate a *cis*-configuration for the surfactant–chromium(III) complexes.

3.1.3. ^{1}H NMR spectra. The ^{1}H NMR spectra offer proof of the configuration of the isomers in solution. For the *cis* complexes, due to lower symmetry, methylene protons of ethylenediamine show a more complex absorption at 2.2–2.8 ppm (Supplementary material). The methylene protons of the long-chain moieties (dodecylamine/cetylamine) give rise to a multiplet usually at 1.2–1.8 ppm, whereas the terminal methyl gives a triplet at 0.85 ppm. The ^{1}H NMR spectral data for the chromium(III)–triethylenetetramine complexes exhibit signals in the region 2.3–3.0 ppm, attributable to the $-CH_2$ group of the triethylenetetramine chelate ring. *bis*-Type chromium(III) complexes of 2,2′-bipyridine or 1,10-phenanthroline take only the *cis*-configuration because of repulsion between the ligands. Assignment of the 1,10-phenanthroline and bipyridine complexes were made in a manner similar to their respective parent complexes [39, 40].

3.1.4. Magnetic measurements. Room temperature magnetic susceptibility measurements were carried out using a Cahn (Model 6612) magnetic susceptibility system. The magnetic moments (μ_{eff} in units of Bohr Magnetrons, B.M.) were calculated after incorporating the diamagnetic corrections [41]. The magnetic moments (3.60–3.80 B.M.) are close to the calculated spin-only value (3.87 B.M.) for a d^3 octahedral Cr(III) complex with a substantially $^4A_2$ ground state [42, 43].

3.2. *CMC values*

The CMC values were computed from the slope of [Cr(III)] *versus* specific conductance data. The complex concentration at which the micellization starts was evident from the change in the slope of the plot; that particular concentration is the CMC under the experimental conditions. The CMC values were determined at three different temperatures (303, 308, and 313 K). At all temperatures a break in the conductance *versus* concentration plots, characteristic of micelle formation, was observed. The CMC values were determined by fitting the data points above and below the break to $y = mx + c$ and solving the two equations simultaneously to obtain the point of intersection. Least-squares analysis was employed and correlation coefficients were greater than 0.98 in all cases. Conductivity measurements at three different temperatures were repeated three times and the accuracy of the CMC values (table 2) was found within $\pm 3\%$ error. Figure 1 illustrates the plot for *cis*-$[Cr(en)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$; similar plots (not shown) were obtained for the remaining complexes. On changing from Cl^- to Br^-, CMC decreases, perhaps due to increase in the size of the ion in the coordination sphere, making it more weakly hydrated. Weakly hydrated ions can be adsorbed more readily in the micellar surface that decreases charge repulsion between polar groups facilitating micellization. The CMC decreases due to an increase in the hydrophobic character of the molecule in the coordination sphere with that of dodecyl/cetylamine.

Table 2. CMC values of chromium(III) metallosurfactants in aqueous solution.

Surfactants	CMC ($mol\,dm^{-3}$) 303 K	308 K	313 K	ΔG^0_m ($kJ\ mol^{-1}$)	ΔH^0_m ($kJ\,mol^{-1}$)	$T\Delta S^0_m$ ($kJ\,mol^{-1}$)
cis-$[Cr(en)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	3.5×10^{-4}	7.4×10^{-4}	9.3×10^{-4}	-38.0 ± 0.4	-19.4 ± 0.2	18.6 ± 0.1
cis-$[Cr(en)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$	2.1×10^{-5}	3.0×10^{-5}	5.2×10^{-5}	-51.5 ± 0.2	-34.9 ± 0.1	16.6 ± 0.3
cis-α-$[Cr(trien)(C_{12}H_{25}NH_2)_2](ClO_4)_3$	1.1×10^{-4}	2.4×10^{-4}	3.7×10^{-4}	-43.6 ± 0.1	-17.8 ± 0.2	25.8 ± 0.1
cis-α-$[Cr(trien)(C_{16}H_{33}NH_2)_2](ClO_4)_3$	9.6×10^{-6}	1.3×10^{-5}	2.0×10^{-5}	-55.3 ± 0.3	-28.4 ± 0.3	26.9 ± 0.4
cis-$[Cr(bpy)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$	8.2×10^{-4}	9.0×10^{-4}	9.6×10^{-4}	-34.0 ± 0.2	-12.2 ± 0.1	21.8 ± 0.1
cis-$[Cr(bpy)_2(C_{12}H_{25}NH_2)Br](ClO_4)_2$	6.5×10^{-4}	6.9×10^{-4}	7.4×10^{-4}	-35.1 ± 0.2	-14.6 ± 0.4	20.5 ± 0.2
cis-$[Cr(bpy)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	1.0×10^{-4}	1.7×10^{-4}	2.3×10^{-4}	-44.1 ± 0.1	-16.0 ± 0.5	28.1 ± 0.5
cis-$[Cr(bpy)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$	5.6×10^{-5}	6.4×10^{-5}	7.1×10^{-5}	-46.9 ± 0.1	-20.7 ± 0.1	26.2 ± 0.1
cis-$[Cr(bpy)_2(C_{16}H_{33}NH_2)Br](ClO_4)_2$	3.8×10^{-5}	4.3×10^{-5}	6.2×10^{-5}	-48.7 ± 0.1	-29.0 ± 0.2	19.7 ± 0.2
cis-$[Cr(bpy)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$	8.4×10^{-6}	1.5×10^{-5}	2.4×10^{-5}	-55.9 ± 0.3	-32.4 ± 0.1	23.5 ± 0.3
cis-$[Cr(phen)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$	7.3×10^{-4}	8.1×10^{-4}	8.7×10^{-4}	-34.5 ± 0.4	-11.2 ± 0.1	23.3 ± 0.1
cis-$[Cr(phen)_2(C_{12}H_{25}NH_2)Br](ClO_4)_2$	6.0×10^{-4}	6.6×10^{-4}	7.0×10^{-4}	-35.7 ± 0.5	-12.9 ± 0.2	22.8 ± 0.2
cis-$[Cr(phen)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	0.7×10^{-4}	1.3×10^{-4}	1.9×10^{-4}	-45.8 ± 0.1	-13.8 ± 0.4	32.0 ± 0.2
cis-$[Cr(phen)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$	4.1×10^{-5}	4.7×10^{-5}	5.3×10^{-5}	-48.3 ± 0.2	-17.7 ± 0.1	30.6 ± 0.1
cis-$[Cr(phen)_2(C_{16}H_{33}NH_2)Br](ClO_4)_2$	2.4×10^{-5}	3.0×10^{-5}	4.4×10^{-5}	-50.9 ± 0.7	-21.4 ± 0.3	29.5 ± 0.2
cis-$[Cr(phen)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$	6.6×10^{-6}	7.5×10^{-6}	9.1×10^{-6}	-57.1 ± 0.1	-24.6 ± 0.2	32.5 ± 0.1

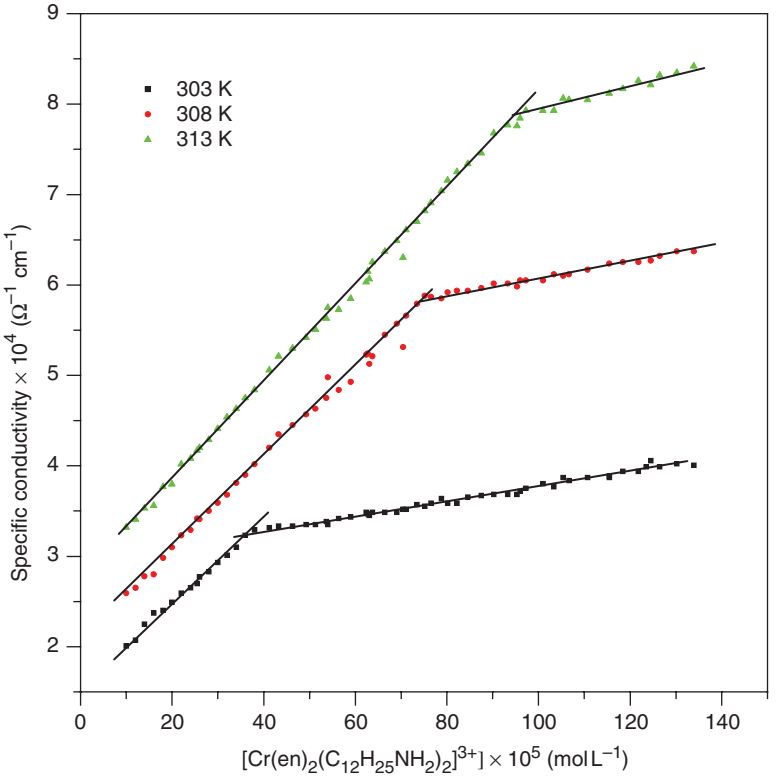


Figure 1. Electrical conductivity *vs.* [Cr(III)] in aqueous solution.

3.3. *Thermodynamics of micellization*

Study of CMC *versus* temperature is often undertaken to obtain information on hydrophobic and head group interactions from thermodynamic parameters of micelle formation. Two models are generally used, the mass-action or equilibrium model and the phase separation or pseudo-phase model. The mass-action model assumes that an equilibrium exists between the monomeric surfactant and the micelles. The phase separation model assumes that the aggregates have their counterions in a separate phase [44–46]. According to these models, the standard Gibbs free energy of micelle formation per mole of monomer, ΔH^0_m, is given by

$$\Delta G^0_m = RT(2 - \alpha_{ave}) \ln \mathrm{CMC} \quad (1)$$

where R, T, and α_{ave} are gas constant, absolute temperature, and average degree of micellar ionization, respectively.

The enthalpy of micelle formation can be obtained by applying the Gibbs–Helmholtz equation to equation (1)

$$\Delta H^0_m = -RT^2(2 - \alpha_{ave})\, \mathrm{d} \ln \mathrm{CMC}/\mathrm{d}T \quad (2)$$

Once the Gibbs free energy and the enthalpy of micelle formation are obtained, the entropy of micelle formation can be determined. The thermodynamic parameters of micellization for the cationic surfactant are compiled in table 2. More negative Gibbs

Table 3. Antimicrobial activities of chromium(III) metallosurfactants.

	Diameter of zone inhibition (mm)						
	Antibacterial activity				Antifungal activity		
Surfactants	*E. coli*	*S. aureus*	*P. vulgaris*	*B. subtilis*	*Trichoderma* sp.	*Aspergillus niger*	*C. albicans*
cis-$[Cr(en)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	10	14	17	14	12	13	12
cis-$[Cr(en)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$	10	16	12	13	12	11	10
cis-α-$[Cr(trien)(C_{12}H_{25}NH_2)_2](ClO_4)_3$	12	17	15	12	8	9	8
cis-α-$[Cr(trien)(C_{16}H_{33}NH_2)_2](ClO_4)_3$	13	15	11	12	10	10	7
cis-$[Cr(bpy)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$	11	10	10	12	10	10	11
cis-$[Cr(bpy)_2(C_{12}H_{25}NH_2)Br](ClO_4)_2$	13	13	14	15	11	12	13
cis-$[Cr(bpy)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	9	12	12	9	8	8	7
cis-$[Cr(bpy)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$	10	11	12	11	11	9	9
cis-$[Cr(bpy)_2(C_{16}H_{33}NH_2)Br](ClO_4)_2$	11	14	10	13	11	9	10
cis-$[Cr(bpy)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$	8	9	10	9	8	8	7
cis-$[Cr(phen)_2(C_{12}H_{25}NH_2)Cl](ClO_4)_2$	11	13	12	11	10	13	10
cis-$[Cr(phen)_2(C_{12}H_{25}NH_2)Br](ClO_4)_2$	12	12	14	12	12	11	12
cis-$[Cr(phen)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$	8	11	9	9	7	6	9
cis-$[Cr(phen)_2(C_{16}H_{33}NH_2)Cl](ClO_4)_2$	13	10	14	11	12	12	13
cis-$[Cr(phen)_2(C_{16}H_{33}NH_2)Br](ClO_4)_2$	12	16	12	12	11	10	12
cis-$[Cr(phen)_2(C_{16}H_{33}NH_2)_2](ClO_4)_3$	9	10	8	10	9	7	9
Standard	20	17	20	18	12	13	15

Standard – Ciprofloxacin for bacteria and clotrimazole for fungi.
Solvent – DMSO (showed nil effect against the microorganisms under test).

free energy of micellization indicates more favored micellization for the system under study compared to hexadecyltrimethylammonium bromide ($CMC = 9.0 \times 10^{-4}\,mol\,dm^{-3}$). Since changes of CMC with temperature are small, the values of ΔH^0_m and ΔS^0_m should be considered as only approximate. Nusselder and Engberts [47] have suggested that for negative ΔH^0_m values, London-dispersion forces play a major role in micelle formation. Positive values of ΔS^0_m clearly indicate that the micellization of the studied surfactants in aqueous solution is governed mainly by hydrophobic interactions between the surfactant cations resulting in the breakdown of the water surrounding the hydrophobic groups and indicates that cationic surfactant formation is entropy driven. The observed increase in the entropy indicates that increasing head group polarity favors micellization. The CMC values for Cr^{III} metallosurfactants in the present study are very low compared to that of simple organic surfactants [33–35], suggesting that these metal surfactant complexes have more capacity to form aggregates compared to those of ordinary organic surfactants. Introduction of a metal complex to the hydrophilic part of the amphiphile can remarkably enhance aggregation.

3.4. *Antibacterial and antifungal screening*

In vitro cytotoxicity of chromium(III) metallosurfactants was screened to evaluate the biological activity against the certain human pathogenic bacteria and fungi (table 3). The test solutions were prepared in DMSO. The microbes used were the Gram +ve, Gram −ve bacteria, and fungi. The complexes exhibit considerable activity under identical experimental conditions; double chain metallosurfactants show greater activity

than the corresponding single chain metallosurfactants. The complexes are more active against fungi than the standard antifungal drug, clotrimazole.

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