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Synthesis and Characterisation of Cationic Surfactant Cobalt(III) Complexes Containing 3,8-Dimethyl-5,6-Benzo-4,7-Diaza Deca-3,7-diene-2,9-dione Dioxime

M.N. ARUMUGHAM†, K. SANTHAKUMAR and S. ARUNACHALAM*
Department of Chemistry, Bharathidasan University, Tiruchirappalli-620 024, India
E-mail: arunasurf@yahoo.com

A number of mixed ligand complexes of the type *trans*-[Co(DODOHbzo)(AM)(X)]$(ClO_4)_2$ and [Co(DODOHbzo)$(AM)_2$]$(ClO_4)_2$ where (DODOHbzo = mono anion of 3,8-dimethyl-5,6-benzo-4,7-diaza deca-3,7-diene-2,9-dioxime, AM = propylamine or dodecylamine and X = Cl^- or I^-) have been synthesized and characterized. The electronic absorption spectra, IR and NMR (^1H) spectra indicate the *trans*- configuration for the isolated complexes.

Key words: **Cobalt(III), Complexes, Dioxime.**

INTRODUCTION

The discovery of vitamin-B_{12} like chemical properties of complexes of bis(dimethylglyoximato) cobalt, *i.e.*, the cobaloximes, by Schrauzer and Kohnle[1] demonstrated the feasibility of this approach and in turn stimulated further research on vitamin-B_{12} like compounds. Subsequently, numerous other cobalt chelates were tested as possible vitamin-B_{12} models, especially propylene and ethylenediamine Schifft's bases of 2,3-butanedione monoxime and Schiff's bases derived from salicylaldehyde and acetylacetone, particularly by Costa and coworkers[2–7]. Among the models reported, Costa's cobalt chelates of **(I)** its ethylenediamine analogue **(II)**, and their related ligand **(III)**, are the only monoanionic macrocyclic dioxime ligands. Mathur and Narang[8] synthesised the ligand, 3,8-dimethyl-5,6-benzo-4,7-diaza deca-3,7-dieno-2,9-diene dioxime $(DOH)_2$bzo **(IV)** as a gravimetric reagent for the estimation of nickel(II). Subsequently, several cobalt(III) complexes of this ligand were prepared[9, 10] and characterized as possible models for vitamin-B_{12}.

In this paper, synthesis of some surfactant complexes having core structure of this type are described. Electronic and IR spectra of these complexes are reported along with those of their ordinary analogues which have also been synthesised for comparison. Also measurements on Critical Micelle Concentration (CMC) values are discussed.

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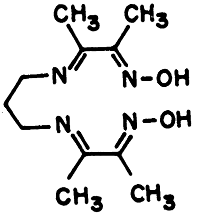
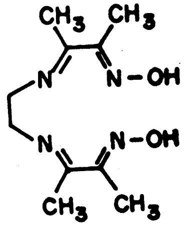
†Department of Chemistry, Vellore Institute of Technology, Deemed University, Vellore, Tamil Nadu. India.


(I)
$(DOH)_2$ pn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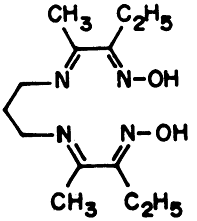
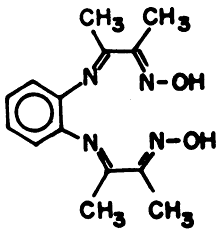

(III)
$C_2(DOH)_2$ pn


(IV)
$(DOH)_2$ bzo

EXPERIMENTAL

Cobalt(II) chloride hexahydrate, cobalt(II) nitrate hexahydrate, potassium iodide, 2,3-butanedione monoxime and *o*-phenylenediamine were BDH reagents. Propylamine and dodecylamine were supplied by Merck. The ^1H NMR spectra were recorded in $CDCl_3$. The ligand 3,8-dimethyl-5,6-benzo-4,7-diaza deca-3,7-diene-2,9-dione dioxime $(DOH)_2$bzo was prepared by methods described in the literature[8].

Syntheses of Complexes

Trans-$[Co(DODOHbzo)(DA)_2](ClO_4)_2$ (1)

The ligand $(DOH)_2$bzo (0.823 g, 3 mmol) was added in small lots to $Co(NO_3)_2 \cdot 6H_2O$ in ethanol (30 mL) (0.873 g, 3 mmol) followed by a solution of dodecylamine (1.38 mL, 6 mmol) in ethanol (5 mL). Then saturated solution of sodium perchlorate (5 mL) was added to the above solution and the mixture was refluxed for 30 min and then cooled to room temperature. When the solution was concentrated, the dark brown complex was separated out and it was filtered off, washed with ether and dried in a vacuum desiccator. The complex was recrystallised from methanol (yield 60%).

Trans-$[Co(DODOHbzo)(DA)Cl](ClO_4)$ (2)

The ligand $(DOH)_2$bzo (0.274 g, 1 mmol) was added in small lots to $CoCl_2 \cdot 6H_2O$ in ethanol (10 mL) (0.24 g, 1 mmol) followed by a solution of dodecylamine (0.23 mL, 1 mmol) in ethanol (5 mL) with stirring. After that a saturated solution of sodium perchlorate (5 mL) was added to the above mixture and it was refluxed for 30 min and then cooled. When the solution was concentrated, the dark brown complex was separated out and it was filtered off, washed with ether and dried in a vacuum desiccator. The complex was recrystallised from methanol (yield 50%).

Trans-[Co(DODOHbzo)(DA)I](ClO_4) (3)

The ligand $(DOH)_2bzo$ (0.548 g, 2 mmol) was added in small lots to $Co(NO_3)_2 \cdot 6H_2O$ in ethanol (20 mL) (0.873 g, 3 mmol) and then potassium iodide (0.332 g, 2 mmol) was added to it followed by a solution of dodecylamine (0.46 mL, 2 mmol) in ethanol (5 mL) with stirring. After that a saturated solution of sodium perchlorate (5 mL) was added to the above mixture and it was refluxed for 30 min and then cooled. When the solution was concentrated, the dark brown complex was separated out and it was filtered off, washed with ether and dried in a vacuum desiccator. The complex was recrystallised from methanol (yield 55%)

Trans-[Co(DODOHbzo)$(PA)_2$]$(ClO_4)_2$ (4)

This complex was synthesised by adopting the same method as described in complex (1) except that in place of dodecylamine, propylamine was used (yield 55%).

Trans-[Co(DODOHbzo)(PA)Cl](ClO_4) (5)

This complex was synthesised by adopting the same method as described in complex (2) except that in place of dodecylamine, propylamine was used (yield 40%).

Trans-[Co(DODOHbzo)(PA)I](ClO_4) (6)

This complex was synthesised by adopting the same method as described in complex (3) except that in place of dodecylamine, propylamine was used (yield 60%).

Physical measurements were done by the methods described earlier.[11] The ^1H NMR spectra were recorded in $CDCl_3$.

RESULTS AND DISCUSSION

The analytical data and the characteristic electronic absorption maxima of the complexes in water are given in Table-1. The absorption in the region 230–250 nm have been assigned to intra-ligand $n \rightarrow \pi^*$ transitions of the coordinated ligand. The absorption band in the region 300–320 nm has been attributed to transitions involving the metal oxime grouping[12]. The comparatively intense absorptions in the region 275–305 nm are attributed to Co(III), $n \rightarrow \pi^*$ (DOH), MLCT transitions. The ligand field spectra of the complexes show a band centred around 430–450 nm, which is found to be much defined for the iodo complexes. This low energy band may be assigned to spin allowed $^1Ag_{1g} \rightarrow {}^1T_{1g}$ transitions[13]. The other spin-allowed $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is masked by the intense charge-transfer bands occurring in the region 300–370 nm.

TABLE-1
ANALYTICAL, ELECTRONIC ABSORPTION SPECTRAL DATA AND CRITICAL MICELLE CONCENTRATION VALUES FOR COBALT(III) COMPLEXES

Compound	Found (Calcd.)%			λ_{max} nm (ε) (M^{-1} cm^{-1})	CMC values in water at 30°C (mol dm^{-3})
	Co	Cl/I	N		
Trans-[Co(DODOHbzo)(DA)$_2$](ClO)$_2$	6.2 (6.6)	7.9 (8.2)	9.5 (9.7)	237 (26219); 314 (11186)	3.3×10^{-5}
Trans-[Co(DODOHbzo)(DA)Cl](ClO$_4$)	8.7 (9.0)	10.5 (10.9)	10.4 (10.7)	236 (37994); 314 (9642)	3.0×10^{-4}
Trans-[Co(DODOHbzo)(DA)I](ClO$_4$)	7.7 (7.9)	16.6 (17.0)	9.1 (9.4)	237 (32658); 314 (9642)	3.0×10^{-4}
Trans-[Co(DODOHbzo)(PA)$_2$](ClO$_4$)$_2$	8.7 (9.1)	10.5 (10.9)	12.6 (12.9)	238 (18150); 315 (10300)	-
Trans-[Co(DODOHbzo)(PA)Cl](ClO$_4$)	10.9 (11.2)	13.0 (13.5)	13.0 (13.3)	238 (18986); 314 (14234)	-
Trans-[Co(DODOHbzo)(PA)I](ClO$_4$)	9.1 (9.5)	20.0 (20.5)	10.9 (11.3)	238 (26941); 314 (11626)	-

The IR absorption frequencies show the main bands due to the coordinated macro ligand and the alkylamine ligand. The more prominent IR bands are located almost in the same position in all the complexes and not much effective variation is detected. A comparison of the IR spectra of these complexes is made with those of the free ligand. The infrared spectrum of the ligand shows no characteristic absorption assignable to either C=O or NH_2 function. This confirms the formation of ligand. The sharp medium intensity band at 1575 cm^{-1} is attributed to ν(C=N)[14] while a similar band at 1630 cm^{-1} is assigned to ν(C=C)[15]. The strong as well as sharp band around 1220 cm^{-1} is due to the N—O stretching vibration[16, 17].

The broad medium-intensity bands appearing around 3477 cm^{-1} are due to alkylamine NH_2 vibrations[11]. The two bands appearing at about 3120 and 3217 cm^{-1} are due to the CH stretching vibrations[18]. The broad band around 2958 cm^{-1} is assignable to ν(OH)[19]. The very strong band of medium broadness at 1557 cm^{-1} and the weak band at 1430 cm^{-1} are assigned to the ring modes or *ortho*-disubstituted benzene[20]. The sharp bands of medium intensity at 1370 and 1447 cm^{-1} are due to the symmetric and asymmetric deformation vibrations respectively of the methyl group[16].

The strong bands appearing at 1237, 1087 and 1003 cm^{-1} are assignable to ν(C—C), ν(C—N) or coupled vibration between these modes respectively.

The ^1H NMR spectra of all the complexes show a sharp singlet at 1.23 ppm for the 12 methyl protons of the equatorial ligand. This indicates that all the complexes are in *trans-* configuration. The aromatic protons appear as broad multiplets centered between 7.5 and 8 ppm. The methyl protons of dodecylamine appear as singlet at 0.87 ppm. The amine (—NH_2) protons of dodecylamine appear as sharp singlet at 2.75 ppm. The methylene (—CH_2) protons of dodecylamine appear in the region of 1.9 to 1.2 ppm. The hydrogen-bonded proton signal is not detected.

Determination of Critical Micelle Concentration Values (CMC)

Plots of specific conductance *vs.* concentration of the aqueous solution of various surfactant complexes indicate that there is an intersection point in each for each complex (Fig. 1) showing the formation of aggregation similar to the phenomena observed in other well known organic surfactants like cetyltrimethylammonium bromide[21]. The critical micelle concentration values are taken from the concentration values corresponding to the intersection points in the plots and these CMC values are given in Table-1. An interesting and useful aspect is that the critical micelle concentration values observed for all these complexes are very low compared to that of the simple organic amphiphilic ligand, dodecylammonium chloride (CMC = 1.5×10^{-2} mol dm^{-3})[22]. Thus it is concluded that these metal surfactant complexes have also more capacity to associate themselves forming aggregates compared to those of the ordinary synthetic organic surfactants. This suggests that the introduction of a metal complex to the hydrophilic part of the amphiphile can remarkably enhance the ability of aggregation.

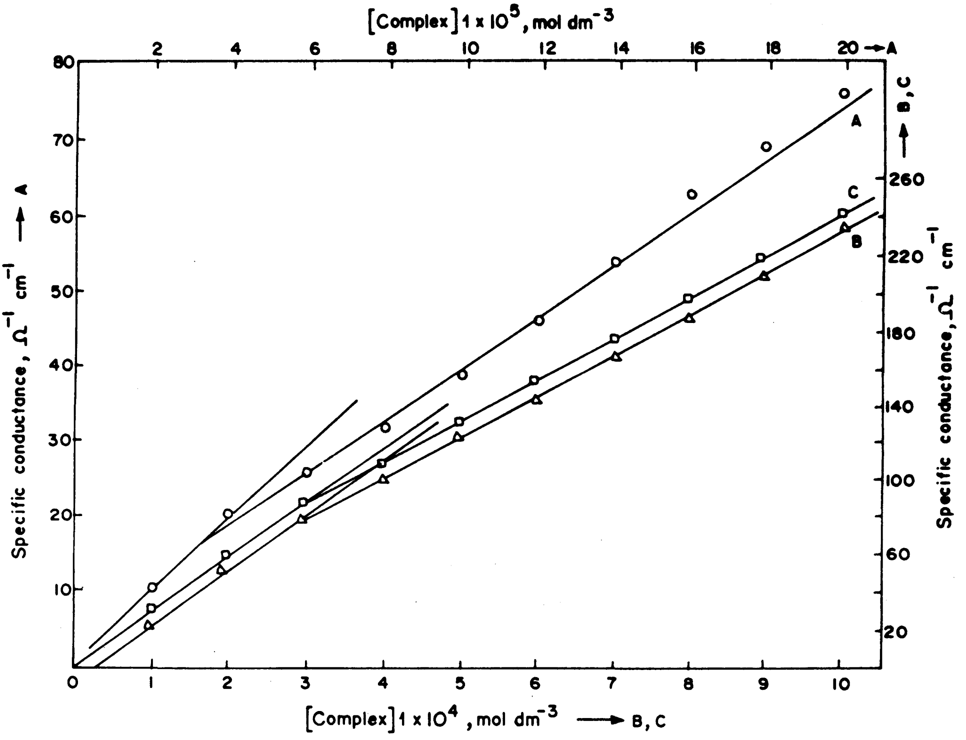


Fig. 1. Plot of specific conductance *vs.* concentration at 30°C; critical micelle concentration of (A) *trans*-$[Co(DODOHbzo)(DA)_2](ClO_4)_2$; (B) *trans*-$[Co(DODOHbzo)(DA)(Cl)]ClO_4$; (C) *trans*-$[Co(DODOHbzo)(DA)I]ClO_4$ complexes.

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