

The Novel Lyotropic Liquid Crystalline Phase of the Dinuclear Metal Complex $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]\dagger$

Norio Koine,^{* a} Masayasu Iida,^b Takako Sakai,^b Narumi Sakagami^c and Sumio Kaizaki^c

^a Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan

^b Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630, Japan

^c Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, 560, Japan

The dinuclear metal complex $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ forms a lyotropic liquid crystalline phase with water, even in dilute solution, and the mesophase is proposed to have a chiral lamellar structure consisting of monolayers of molecules, which are formed by extensive stackings between the phen groups and separated by layers of water.

A wide range of organic and biological compounds form lyotropic crystalline phases.¹ However no lyotropic mesophase of a metal complex has been reported, although many thermotropic examples are known.² We now report the formation of a lyotropic mesophase by the chiral dinuclear chromium(III) complex shown in Fig. 1.

The corresponding ammonium phen and barium bpy[†] complexes have previously been prepared and studied.³ Recently, a crystal structure determination has been carried out on the corresponding acid bpy complex.[‡]

At concentrations above *ca.* $0.006 \text{ mol dm}^{-3}$ at 20°C aqueous solutions of the sodium phen complex^{4§} appear slightly turbid and proved to be birefringent when viewed in a polarizing microscope. These facts indicate the formation of a

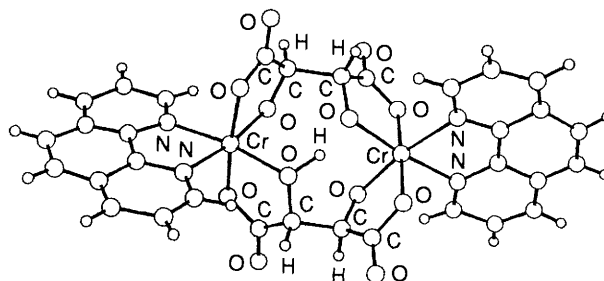


Fig. 1 The molecular structure proposed for $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$. The conformational geometry was taken to be the same as that of the corresponding acid bpy complex.[‡]

[†] phen = 1,10-phenanthroline; tart = $\text{C}_4\text{H}_2\text{O}_6^{4-}$; bpy = 2,2'-bipyridine.

[‡] N. Koine, N. Sakagami and S. Kaizaki, the 61st National Meeting of the Chemical Society of Japan, Yokohama, March 1991, Abstr., No. 1P07. The X-ray crystal structure analysis of $\text{H}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{bpy})_2] \cdot 3.5\text{H}_2\text{O}$ reveals that the fundamental structure of the complex ion is consistent with that proposed in earlier reports (refs. 3 and 4). The unit cell contains two crystallographically independent complexes slightly different in their conformations and the two bpy ring planes are twisted with a dihedral angle of nearly a right angle (73.8 and 75.8°) to each other around the molecular axis passing through the two chromium atoms.

[§] The sodium phen complex used here was obtained as hemitridecahydrate columnar crystals by crystallization from hot water-dimethylformamide (1:1) solution, stimulated by adding a small amount of aqueous sodium chloride, but not as the reported pentahydrate plates (ref. 4).

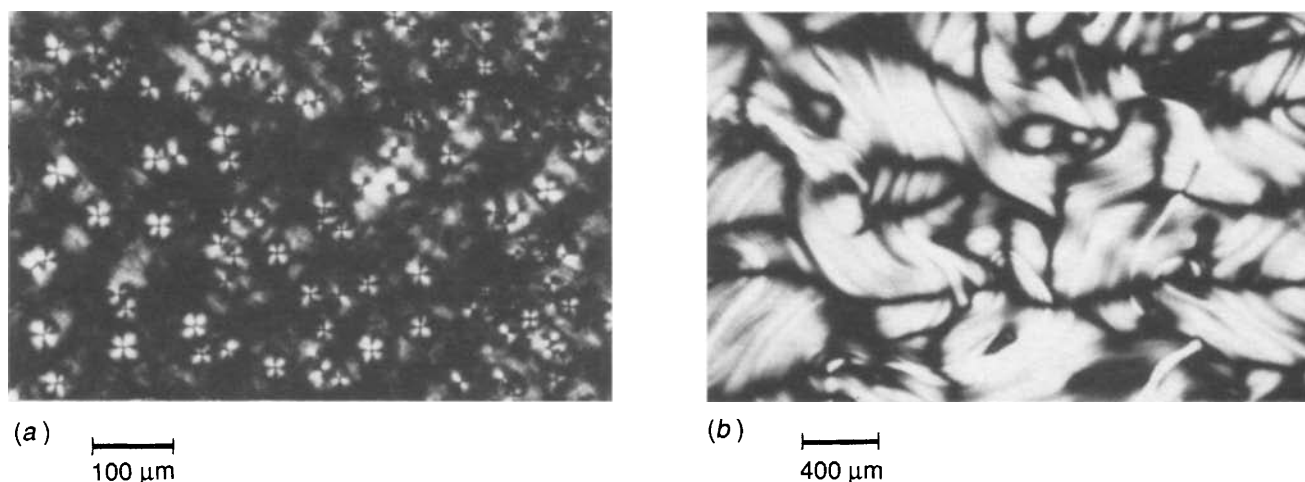


Fig. 2 The optical textures of aqueous solutions of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ viewed between crossed polars. This sample was obtained by allowing uncovered drops of a hot solution containing $0.008 \text{ mol dm}^{-3}$ on a glass slide to cool to room temperature. (a) A two-phase region containing spherulites of mesophase emerging from the isotropic solution. (b) The bulk mesophase with a striped fan texture.

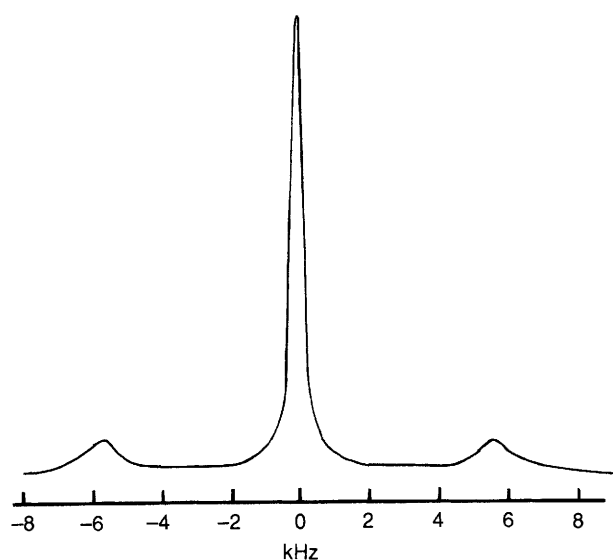


Fig. 3 High-resolution ^{23}Na NMR (71.36 MHz) spectrum of 0.06 mol dm^{-3} aqueous solution of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ at 27°C

lyotropic liquid crystalline phase. Hot dilute isotropic solutions (*ca.* 0.06 mol dm^{-3}) become birefringent on cooling to room temperature in a reversible way, whilst more concentrated solutions (up to 0.10 mol dm^{-3} ; the highest concentration examined) are birefringent up to 100°C . Fig. 2 shows two characteristic optical textures of the mesophase. Further evidence for the formation of a liquid crystalline phase is given by quadrupole splitting in the ^{23}Na NMR spectrum (Fig. 3) which indicates the presence of sodium ions in an anisotropic environment.

Even dilute mesophase samples have unusually high viscosity. This increases further with concentration and above levels of $0.065 \text{ mol dm}^{-3}$ (at 20°C) they have almost no fluidity. Furthermore, the mesophase samples are homogeneous and have strong spinnability (highest value at *ca.* $0.055 \text{ mol dm}^{-3}$), regardless of the concentrations. There seems to be a high level of molecular aggregation with the solvent water, possibly caused by interactions between the phen groups.

Two characteristic CD spectra of the birefringent phase are shown in Fig. 4 and that of the isotropic solution^{4,5} is given for comparison. The high intensity of the peaks in the region $<400 \text{ nm}$ is worth noting. The positions, signs and intensities

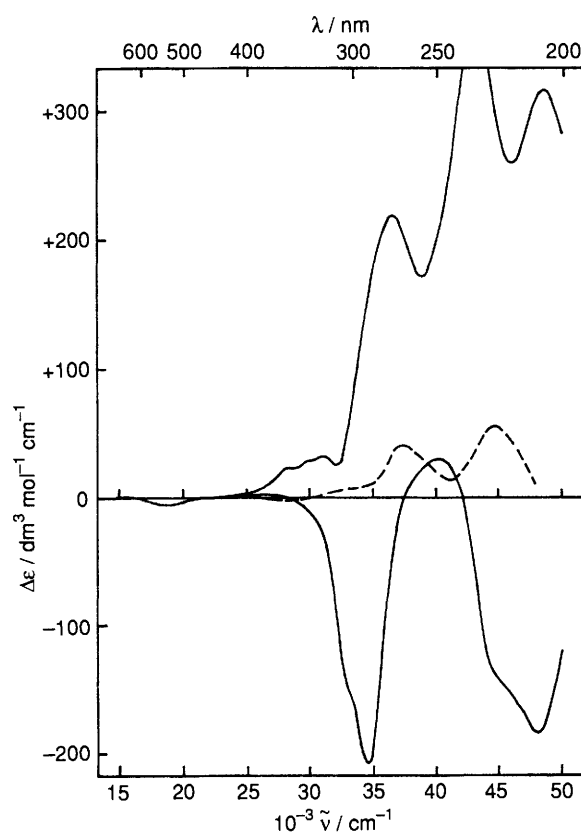


Fig. 4 CD spectra of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ at room temperature. Solid lines: characteristic spectra of $0.015 \text{ mol dm}^{-3}$ aqueous solutions with a change in position of the sample in a quartz cell with a demountable window [$\Delta\epsilon$ was referred to $\Delta\epsilon_{\text{max}}$ (-8.11 , ref. 3) at 546 nm for the isotropic solution]. Broken line: isotropic solution in H_2O -dimethylformamide (1:1).

of the maxima were sensitive to positional changes of the sample. This indicates that the sample contains structural domains of size comparable to the beam width. However, the random orientation of the sample makes it impossible to explain the CD behaviour in detail. The large magnitude of $\Delta\epsilon$ may result from the selective reflection of circularly polarized light of one handedness caused by the macroscopic twist of a cholesteric (*i.e.*, twisted nematic)⁶ or chiral smectic⁷ type of structure.

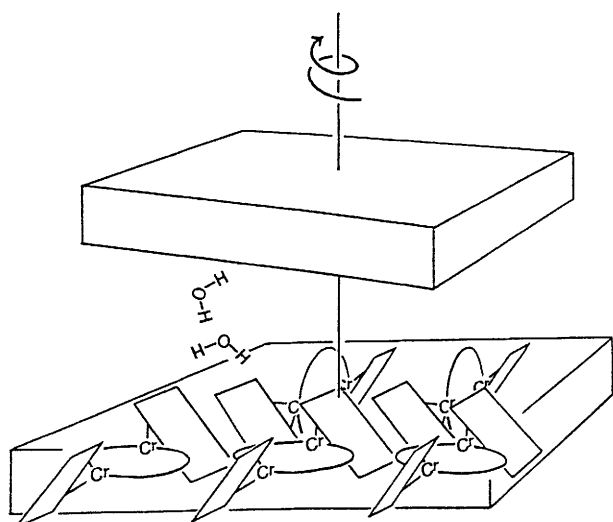


Fig. 5 The proposed chiral lamellar structure of the mesophase. In each monolayer the molecules lie parallel to each other and parallel to the layer surfaces. The bridging tartrate groups cause the layer surfaces to be sufficiently hydrophilic for a lyotropic mesophase to be formed.

At first sight, the molecular structure of this complex does not appear to be a very promising candidate for mesophase formation. It is not recognisably polar, without the hydrophilic head and hydrophobic alkyl chain tail of conventional amphiphiles like soaps and detergents, nor is it recognisably of

the chromonic type with a central planar aromatic region and peripheral solubilising groups. We therefore suggest that the mesophase formed is of a novel type. The model we propose is shown in Fig. 5. We have no direct evidence concerning the molecular arrangement and the suggestion is based on the crystal structure of the corresponding acid bpy complex.[‡] The overall structure is of the lamellar type with monolayers of metal complex ions interleaved with layers of water. The molecules lie with their long axes in the plane of the monolayer (neither perpendicular nor near-perpendicular as in conventional lamellar and smectic phases). Each monolayer is formed by extensive stackings of the phen groups where both sides of all the phen rings are involved in the layer formation. As a result, the tartrate bridges presumably create sufficient hydrophilic regions on the layer surface. The proposed model appears to explain the unprecedented formation of the lyotropic liquid crystals of the phen complex.

Received, 12th June 1992; Com. 2/03104C

References

- 1 H. Kelker and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, 1980.
- 2 N. Hoshino, A. Kodama, T. Shibuya, Y. Matsunaga and S. Miyajima, *Inorg. Chem.*, 1991, **30**, 3091.
- 3 S. Kaizaki, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 2207; 1970, **43**, 1100.
- 4 G. L. Robbins and R. E. Tapscott, *Inorg. Chem.*, 1976, **15**, 154.
- 5 S. F. Mason, *Inorg. Chim. Acta*, 1968, **2**, 89.
- 6 C. Robinson, *Tetrahedron*, 1961, **13**, 219.
- 7 T. Tachibana, T. Mori and K. Hori, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1714.