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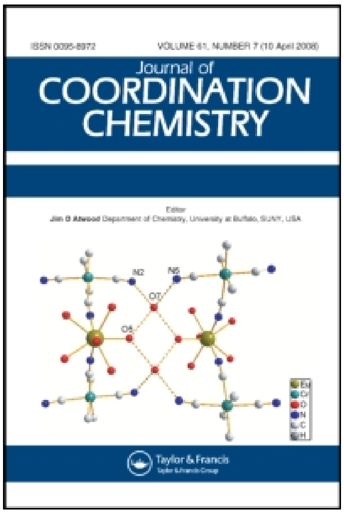

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

BIS(TETRASULFOPHTHALOCYANINATO)SAMARIUM(III)

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To cite this Article Kasuga, K. and Tsutsui, M.(1981) 'BIS(TETRASULFOPHTHALOCYANINATO)SAMARIUM(III)', Journal of Coordination Chemistry, 11: 3, 177 — 178
To link to this Article: DOI: 10.1080/00958978108079066
URL: http://dx.doi.org/10.1080/00958978108079066

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J. Coord. Chem., 1981, Vol. 11, pp. 177–178
0095-8972/81/1103-0177 $06.50/0

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Printed in Great Britain

BIS(TETRASULFOPHTHALOCYANINATO)SAMARIUM(III)

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(Received April 16, 1981)

Bis (tetrasulfophthalocyaninato)samarium(III) was synthesized and identified by means of the elemental analysis and the spectrometry.

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INTRODUCTION

The synthesis of water-soluble metallophthalocyanine complexes has been of recent interest to study a solution chemistry of phthalocyanine compounds.[1] For instance, sulfonated cobalt(II)phthalocyanine was used for catalytic oxidation of thiol compounds.[2] Reversible addition of molecular oxygen to iron(II)tetrasulfophthalocyanine in aqueous solution has also been investigated.[3] We report here the synthesis and some properties of sandwich-type bis(tetrasulfophthalocyaninato)samarium(III).

EXPERIMENTAL

The mixture of triammonium sulfophthalic acid (6.0 g), urea (8.0 g), samarium(III) acetate (1.0 g), and ammonium molybdate (0.5 g) was heated up to 200–210°C with a stirrer and a reflux condenser. After 2 hr, the melted mixture thickened with a dark green color. The crude product was finely ground and washed by methanol and water. Then it was dissolved to *N,N*-dimethylformamide, and three times the volume of water was poured into the filtrate, resulting in the dark green precipitate (this step was repeated twice). The samarium(III) derivative was dried at 110°C for 3 hr *in vacuo* (yields, 1.5 g). Anal. Found: N, 14.89; S, 11.56%. N/S = 2.94. Calcd for $C_{64}H_{60}N_{25}O_{24}S_8 \cdot 18H_2O$ N, 15.27; S, 11.18%. N/S = 3.13. The complex is soluble in *N,N*-dimethylformamide and aqueous ammonia, but only slightly in water.

RESULTS AND DISCUSSION

Since the synthesis of bis(phthalocyaninato)lanthanide(III) complexes was published,[4] interesting studies on their properties have been reported: *e.g.* electrochromism[5] and conductivity.[6] Recently, a molecular structure of bis(phthalocyaninato)neodymium(III) was reported from our laboratory; a neodymium(III) ion occupies a central position between parallel, but staggered phthalocyanine ligands.[7] Moskalev and Kirin also synthesized sulfonated bis(phthalocyaninato)metal(III) complexes of yttrium, gadolinium, and lutetium to study the properties of these compounds in aqueous solution.[8] In their case, the sulfonation had been carried out by heating a powder of the bis(phthalocyaninato)metal(III) complexes at 140–150°C in a stream of argon saturated with sulfur trioxide vapor for 2–3 hr. The complexes obtained contained four or five sulfo-groups. In the present case, the sulfonated compound was synthesized from the mixture of triammonium sulfophthalic acid, urea, and samarium(III) acetate. Ammonium molybdate was also used as a catalyst. Without the catalyst, the mixture did not thicken even above 200°C, nor did it change to the dark green color which is characteristic of the phthalocyanine compounds.

In the visible spectra of aqueous solution, the sulfonated samarium(III) complex shows two intense maximum absorptions at 625 and 670 nm. With an increase of the acidity of the solution, the optical density at 625 nm decreases, while the optical density at 670 nm increases, accompanying an increase of that of the broad absorption band in the wavelength range of 450–550 nm. Adding aqueous ammonia to the solution, the original spectrum is recovered. The spectral change is reversible. This spectral behavior is characteristic of the sandwich-type diphthalocyanine complexes of trivalent lanthanides.[4,9] The results are

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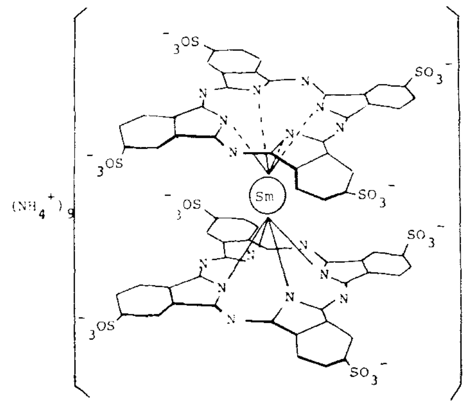
also consistent with the spectral change of bis(disulfophthalocyaninato)lanthanide(III) in aqueous solution studied by Moskalev and Kirin.[8] The suggested model of the present sulfonated complex might be proposed as follows:



Proposed model for ammonium bis(tetrasulfophthalocyaninato)samariumate(III).

ACKNOWLEDGEMENTS

We are grateful for support of this work by the Office of Naval Research (Grant No. 3210) and The Robert A. Welch Foundation (Grant No. A420).

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