

## Supramolecular Motifs in s-Block Metal-Bound Sulfonated Monoazo Dyes: The Case of Orange G

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Solid-state structures of Mg, Sr, Ba, Na<sub>2</sub>, Na<sub>0.8</sub>K<sub>1.2</sub>, NaRb, and Na<sub>1.5</sub>Cs<sub>0.5</sub> complexes of the disulfonated dye 7-hydroxy-8-(phenylazo)-1,3-naphthalenedisulfonic acid, Orange G, are presented. It is shown that the s-block metal salts of the Orange G dianion (**Og**) can be categorized into three structural classes related to those previously proposed for simple monosulfonated azo dyes. All of the structures feature alternate organic/inorganic layering, but whereas the Mg, Ca, and Li complexes are solvent-separated ion-pair species, the Sr and Ba complexes form simple discrete molecules based on metal–sulfonate bonding, and the heavy alkali metal complexes utilize a variety of M–O interactions to form 2- and 3-dimensional coordination networks. These structural differences are rationalized in terms of simple properties of the metals (charge, size, and electronegativity) and the steric demands of the arylsulfonate groups. The Ag<sub>2</sub> complex of Orange G is also structurally characterized, and in contrast to the s-block salts, it is found to exhibit strong Ag  $\pi$  bonds. In confirmation of the above, the crystal structures of [Mg(H<sub>2</sub>O)<sub>6</sub>]-[Og]·3.33H<sub>2</sub>O, [Sr(Og)(H<sub>2</sub>O)<sub>7</sub>]·H<sub>2</sub>O, [Ba(Og)(H<sub>2</sub>O)<sub>7</sub>]·2H<sub>2</sub>O, [Na<sub>2</sub>(Og)(H<sub>2</sub>O)<sub>6.67</sub>], [Na<sub>2</sub>(Og)(H<sub>2</sub>O)<sub>2</sub>(HOEt)], [Na<sub>0.8</sub>K<sub>1.2</sub>-(Og)(H<sub>2</sub>O)<sub>6</sub>]·1.75H<sub>2</sub>O, [NaRb(Og)(H<sub>2</sub>O)<sub>6.5</sub>]·2.375H<sub>2</sub>O, [Na<sub>1.5</sub>Cs<sub>0.5</sub>(Og)(H<sub>2</sub>O)<sub>6</sub>]·0.5H<sub>2</sub>O, and [Ag<sub>2</sub>(Og)(H<sub>2</sub>O)<sub>4</sub>]·H<sub>2</sub>O are presented.

## Introduction

The study of solid-state metal–organic coordination networks has concentrated on transition metal complexes with, until recently, little attention being paid to the systematic study of the equivalent behavior of s-block metals.<sup>1</sup> This is true despite the fact that many such materials are already of commercial importance. Pharmaceuticals, dyes, and pigments typically utilize alkali and alkaline earth cations in preference to transition metals as, in broad terms, the s-block metals have advantages of nontoxicity, cheapness, and often aqueous solubility. Perhaps because of their ubiquity, s-block cations might be ignored by synthetic chemists as mere “spectators”, but where a material’s properties depend on its solid-state structure and the inter-

molecular interactions within that structure, this is obviously far from the truth. Indeed, examples abound of one salt form being preferred over another for practical and commercial purposes.<sup>2</sup> It is our belief that an understanding of the changes in material properties caused by changing the s-block metal cation must be based around consideration of the fundamental properties (charge, size, electronegativity) of these metals and the influence that these properties have on the nature of the resultant solid-state structure.

Illustrating the dearth of knowledge in this area, despite the widespread use of sulfonated azo colorants, there seems to be only four reports of salt structures of para- or meta-sulfonated azo colorants.<sup>3</sup> In our study of simple meta- and para-sulfonated azo dyes, we increased the number of known crystal structures from six to 43 and proposed categorization

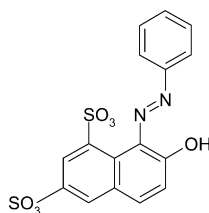
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into three structural classes.<sup>3a</sup> All adopt alternating organic and inorganic layers, reminiscent of the well-studied structures of metal phosphonates;<sup>4</sup> however, the nature of the coordination network differs from class to class. Metal type was found to be the principal factor affecting which class formed, but this can be overridden either by the nature and position of the organic substituents or by solvent choice. Thus, for the para-sulfonated azo dyes, Mg compounds form solvent-separated ion-pair solids (class 1); Ca, Ba, and Li compounds form simple 0- or 1-dimensional coordination networks based on metal-to-sulfonate bonding (class 2); and Na, K, and Rb compounds form more complex or higher-dimensional networks (class 3). Compounds of the meta-sulfonated azo dyes follow a similar pattern, but now Ca species can form either class 1 or class 2 structures, thus illustrating the structural influence of changing the sulfonate position.



The azo tautomer of the Orange G dianion.

One difficulty in examining sulfonated dyes is that they exhibit generally poor crystal growth properties, making single-crystal diffraction studies difficult. An exception is the disulfonated naphthalene-based dye Orange G, 7-hydroxy-8-(phenylazo)-1,3-naphthalenedisulfonic acid, the salts of which are found to grow as robust crystals. This has led to crystallographic characterization of the Orange G dianion (**Og**) both with polyatomic organic cations<sup>5</sup> and as its Mg, Ca, and Li salts.<sup>6</sup> In this article, we present eight new structures of s-block metal compounds of **Og**, together with the structure of its Ag(I) complex. Examination of this family of structures allows structural trends to be elucidated and contrasted to those found previously for para- and meta-monosulfonated azo dyes. This study is therefore of interest as an insight into the solid-state chemistry of colorants and, more generally, as a contribution to our understanding of supramolecular behavior in organo-sulfonates, a field given recent prominence by the work of Shimizu and others.<sup>7</sup>

## Experimental Section

**General.** Samples were obtained by treating aqueous solutions of the commercially available Na salt with an excess of metal halide or Ag(NO<sub>3</sub>). The mixtures were stirred with gentle heating for 1 h. Crude solid, in near-quantitative yields, was obtained by precipita-

tion and filtration. Crystals suitable for single-crystal diffraction, using either conventional laboratory techniques or synchrotron radiation, were grown by recrystallization from water using simple slow cooling or evaporation techniques. The ethanol solvate, Na<sub>2</sub>·(**Og**)·EtOH, was obtained by recrystallizing Na<sub>2</sub>(**Og**) from warm ethanol. No attempt was made to control pH during these recrystallizations, and as a full polymorph screen has not been attempted, the existence of other forms is entirely possible. Certainly, the hydrate forms lose water on heating, and so, anhydrous forms can be easily prepared. Indeed, it is apparent from the microanalytical data given below that partial dehydration upon removal from mother liquor is common. IR spectra were recorded as KBr disks; Raman spectra were recorded from solid placed on microscope slides.

**Crystallography.** Single-crystal diffraction data were recorded on a Nonius Kappa CCD diffractometer, except for compound Ag<sub>2</sub>(**Og**), for which data were obtained at Station 16.2SMX of the Daresbury Synchrotron Radiation Source.<sup>8</sup> Crystals were removed directly from the mother liquors and mounted in inert oils. The structures were refined against *F*<sup>2</sup> to convergence using the SHELXL-97 program.<sup>9</sup> Specific crystallographic data and refinement parameters are given in Table 1.

**Characterization. Mg(Og).** Major IR peaks/cm<sup>-1</sup>: 3457, 2356, 1644, 1557, 1495, 1424, 1383, 1275, 1198, 1137, 1029. Major Raman peaks/cm<sup>-1</sup>: 1593, 1494, 1427, 1331, 1238, 999, 787, 714, 475. Microanalysis/% expected for octahydrate (% found): C 33.43 (33.61), H 4.57 (4.25), N 4.87 (4.98).

**Sr(Og).** Major IR peaks/cm<sup>-1</sup>: 3446, 1634, 1383, 1209, 1045, 681, 528. Microanalysis/% expected for hexahydrate (% found): C 31.92 (32.21), H 3.69 (3.30), N 4.65 (4.78).

**Ba(Og).** Major IR peaks/cm<sup>-1</sup>: 3426, 1552, 1378, 1198, 1034, 656, 476. Microanalysis/% expected for nonahydrate (% found): C 27.94 (27.95), H 3.82 (3.71), N 4.07 (4.06).

**Na<sub>2</sub>(Og).** Major IR peaks/cm<sup>-1</sup>: 3472, 1618, 1552, 1495, 1424, 1383, 1275, 1209, 1029. Major Raman peaks/cm<sup>-1</sup>: 1600, 1499, 1429, 1380, 1335, 1238, 1178, 1000, 786, 714, 473. Microanalysis/% expected for 6.67H<sub>2</sub>O (% found): C 33.57 (33.72), H 4.12 (3.86), N 4.89 (4.91).

**Na<sub>0.8</sub>K<sub>1.2</sub>(Og).** Major IR peaks/cm<sup>-1</sup>: 3436, 1613, 1490, 1454, 1372, 1270, 1183, 1137, 1029, 978. Major Raman peaks/cm<sup>-1</sup>: 1597, 1497, 1430, 1379, 1328, 1238, 943, 788, 717. Microanalysis/% expected for hexahydrate (% found): C 33.14 (33.68), H 3.83 (2.62), N 4.83 (4.91), Na 3.2 (3.5).

**NaRb(Og).** Major IR peaks/cm<sup>-1</sup>: 3434, 1629, 1490, 1370, 1198, 1034, 753, 492. Microanalysis/% expected for nonahydrate (% found): C 28.38 (27.51), H 4.15 (2.26), N 4.15 (4.13), Na 3.4 (3.8).

**Na<sub>1.5</sub>Cs<sub>0.5</sub>(Og).** Major IR peaks/cm<sup>-1</sup>: 3457, 1623, 1383, 1209, 1034, 635. Microanalysis/% expected for 6.5H<sub>2</sub>O (% found): C 30.77 (30.61), H 3.72 (3.23), N 4.48 (4.45), Na 5.5 (5.3).

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**Table 1.** Selected Crystal Parameters and Refinement Data

compound label: chemical identity:	Mg(Og) [Mg(H <sub>2</sub> O) <sub>6</sub> ][Og]·3.33H <sub>2</sub> O	Sr(Og) [Sr(Og)(H <sub>2</sub> O) <sub>7</sub> ]·H <sub>2</sub> O	Ba(Og) [Ba(Og)(H <sub>2</sub> O) <sub>7</sub> ]·2H <sub>2</sub> O	Na <sub>2</sub> (Og) [Na <sub>2</sub> (Og)(H <sub>2</sub> O) <sub>6.67</sub> ]	Na <sub>2</sub> (Og)·EtOH [Na <sub>2</sub> (Og)(H <sub>2</sub> O) <sub>2</sub> (HOEt)]
formula weight	598.84	638.13	1375.70	572.44	534.46
crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> <b>1</b>	<i>P</i> <b>2<sub>1</sub>/n</b>	<i>P</i> <b>1</b>	<i>P</i> <b>1</b>	<i>P</i> <b>2<sub>1</sub>/a</b>
<i>a</i> (Å)	10.2013(1)	8.8032(2)	8.6114(7)	8.9000(3)	9.5614(6)
<i>b</i> (Å)	15.1855(2)	28.2796(7)	11.0894(11)	10.4700(4)	11.4554(10)
<i>c</i> (Å)	25.9510(3)	10.3462(2)	14.6066(15)	13.7350(7)	20.5330(18)
$\alpha$ (deg)	77.880(1)	90	74.033(5)	73.488(2)	90
$\beta$ (deg)	87.437(1)	102.552(1)	78.275(5)	79.289(2)	93.417(2)
$\gamma$ (deg)	76.857(1)	90	69.825(6)	69.499(2)	90
volume (Å <sup>3</sup> )	3827.55(8)	2514.14(10)	1249.7(2)	1144.05(8)	2245.0(3)
<i>Z</i>	6	4	1	2	4
density (Mg m <sup>-3</sup> )	1.559	1.686	1.828	1.662	1.581
$\mu$ (mm <sup>-1</sup> )	0.314	2.385	1.831	0.346	0.335
temperature (K)	123	123	123	123	123
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
reflns collected	50186	23562	17243	8232	9991
reflns unique	17171	5765	4969	4423	5162
<i>R</i> <sub>int</sub>	0.041	0.0626	0.0861	0.0336	0.0306
goodness of fit	1.033	1.028	1.025	1.089	0.981
<i>R</i> [ <i>I</i> > 2s( <i>I</i> )]	0.0462	0.0385	0.0494	0.0452	0.0362
<i>R</i> <sub>w</sub>	0.1121	0.0961	0.1015	0.1275	0.0884

compound label: chemical identity:	Na <sub>0.8</sub> K <sub>1.2</sub> (Og) Na <sub>0.8</sub> K <sub>1.2</sub> (Og)(H <sub>2</sub> O) <sub>6</sub> ·1.75H <sub>2</sub> O	NaRb(Og) [NaRb(Og)(H <sub>2</sub> O) <sub>6.5</sub> ]·2.375H <sub>2</sub> O	Na <sub>1.5</sub> Cs <sub>0.5</sub> (Og) [Na <sub>1.5</sub> Cs <sub>0.5</sub> (Og)(H <sub>2</sub> O) <sub>6</sub> ]·0.5H <sub>2</sub> O	Ag <sub>2</sub> (Og) [Ag <sub>2</sub> (Og)(H <sub>2</sub> O) <sub>4</sub> ]·H <sub>2</sub> O
formula weight	611.32	674.73	624.42	712.20
crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> <b>1</b>	<i>P</i> <b>1</b>	<i>C</i> <b>2/c</b>	<i>P</i> <b>1</b>
<i>a</i> (Å)	8.9908(6)	9.0253(3)	10.0523(1)	8.8702(9)
<i>b</i> (Å)	10.4007(8)	10.6535(4)	18.4467(4)	10.6780(8)
<i>c</i> (Å)	14.9963(12)	15.0770(5)	25.6764(5)	13.2722(9)
$\alpha$ (deg)	83.349(3)	82.303(2)	90	106.435(1)
$\beta$ (deg)	85.054(5)	84.923(2)	92.686(1)	102.805(1)
$\gamma$ (deg)	70.227(5)	69.386(2)	90	108.338(1)
volume (Å <sup>3</sup> )	1309.09(17)	1343.18(8)	4755.99(15)	1075.81(15)
<i>Z</i>	2	2	8	2
density (Mg m <sup>-3</sup> )	1.551	1.668	1.744	2.199
$\mu$ (mm <sup>-1</sup> )	0.479	2.090	1.077	3.131
temperature (K)	120	123	123	100
wavelength (Å)	0.71073	0.71073	0.71073	0.84660
reflns collected	22917	31683	29113	7487
reflns unique	4569	5284	5464	4262
<i>R</i> <sub>int</sub>	0.0687	0.066	0.0471	0.0226
goodness of fit	1.119	1.036	1.049	1.031
<i>R</i> [ <i>I</i> > 2s( <i>I</i> )]	0.0973	0.0617	0.0297	0.0442
<i>R</i> <sub>w</sub>	0.2551	0.1790	0.0648	0.1185

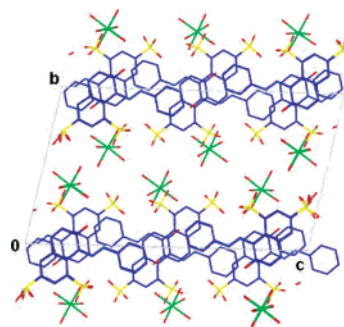
**Ag<sub>2</sub>(Og).** Major IR peaks/cm<sup>-1</sup>: 3457, 1623, 1383, 1209, 1034, 635. Microanalysis poor; bulk sample contaminated with simple inorganic salts.

## Results and Discussion

**Class 1: Solvent-Separated Ion-Pair Solids, Mg, Ca, and Li.** The structures of the Mg, Ca, and Li salts of Orange G were determined previously by Ojala et al.<sup>6</sup> All are of the solvent-separated, ion-pair type, where the **Og** dianion interacts with the [Mg(OH<sub>2</sub>)<sub>6</sub>], [Ca(OH<sub>2</sub>)<sub>7</sub>], or [Li(OH<sub>2</sub>)<sub>4</sub>] cation only through hydrogen-bonding. Repeating these preparations during the course of this work gave the same Ca and Li species as found previously, but the Mg salt differed slightly, with the higher hydrate [Mg(OH<sub>2</sub>)<sub>6</sub>][Og]·3.33H<sub>2</sub>O (as opposed to [Mg(OH<sub>2</sub>)<sub>6</sub>][Og]·2H<sub>2</sub>O) initially being obtained. Figure 1 illustrates both the organic–inorganic layering common to all of these dye complexes and the solvent-separated nature of the class 1 species. The two Mg pseudopolymorphs have broadly similar structural features, the main difference being that the new polymorph

presented here has a double layer of [Mg(OH<sub>2</sub>)<sub>6</sub>] cations between each organic layer, as opposed to the single layer described in ref 6.

In ref 3a, we postulated that an s-block metal's preference for forming bonds to water over forming bonds to SO<sub>3</sub> was

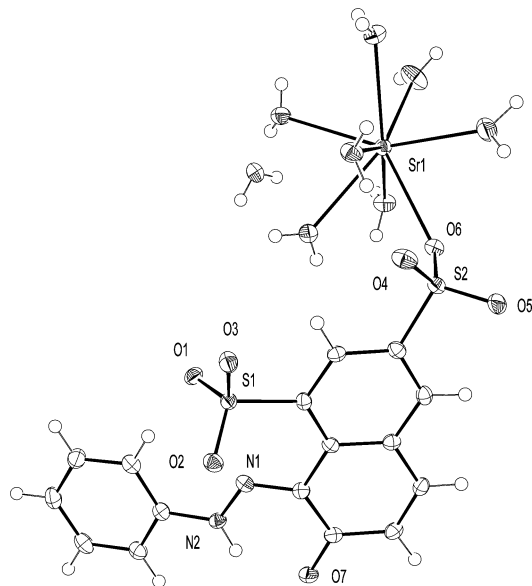


**Figure 1.** Packing diagram of MgOg viewed along the *a* direction. Note the alternating organic (hydrophobic) and inorganic (hydrophilic) layers. Here and in later figures: green, metal; yellow, S; red, O; light blue, N; dark blue, C; H atoms and minor disorder components are not shown for reasons of clarity.

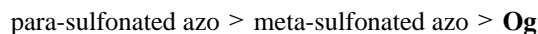
**Table 2.** Coordination Network Types for Various Classes of Sulfonated Azo Dye

metal	electronegativity <sup>a</sup>	structural class		<b>Og</b>
		para-sulfonated azo	meta-sulfonated azo	
Mg	1.31	1	1	1
Ca	1.00	2	1 or 2	1
Li	0.98	2	2	1
Sr	0.95	2	2	2
Na	0.93	3	3	3
Ba	0.89	2	2	2
K	0.82	3	3	3
Rb	0.82	3	3	3
Cs	0.79	3	3	3

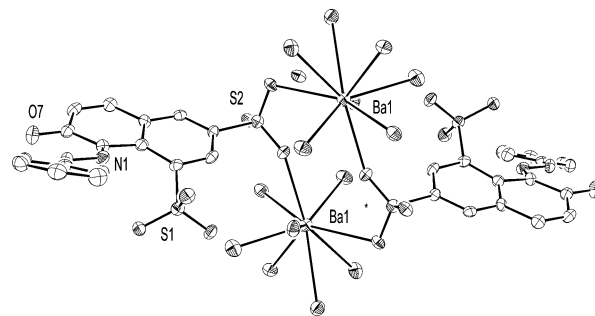
<sup>a</sup> In Pauling units from ref 10.

**Figure 2.** SrOg forms discrete monomers.

related to its electronegativity, which was taken as an expression of the metal's "ionic character". The most electronegative metal (Mg) favors bonding to neutral water, but as the metals become more electropositive and "more ionic", bonding to the formally charged SO<sub>3</sub> groups increasingly dominates. Solvent-separated structures are seen only with Mg for azo dyes with SO<sub>3</sub> para to the azo group but for both Mg and Ca when SO<sub>3</sub> is meta to the azo.<sup>3a</sup> As can be seen in Table 2, Li is the next most electronegative s-block metal after Mg and Ca,<sup>10</sup> so the isolation of [Li(OH<sub>2</sub>)<sub>4</sub>]<sub>2</sub>[Og] indicates a sequential and logical change in ligand behavior and hence structural type. This also implies that the following series of s-block metal binding power is true



**Class 2: Simple SO<sub>3</sub>-M Complexes, Sr and Ba.** In contrast to the Mg, Ca, and Li salts, Sr[Og] does form a metal-sulfonate bonded complex. However, as Sr is only slightly less electronegative than Li, it might be expected to make a low number of sulfonate Sr-O contacts. As can be seen in Figure 2, Sr[Og] does indeed form only one Sr-to-

**Figure 3.** Dimeric structure of BaOg.

sulfonate bond, with the metal coordination geometry being completed by seven terminal water ligands.

Moving down group 2 to Ba further decreases electronegativity and so increases the influence of metal-sulfonate bonding. Ba[Og] utilizes two sulfonate O atoms to form a simple dimer (Figure 3) based around an eight-membered [BaOSO]<sub>2</sub> ring. In both Sr[Og] and Ba[Og], the sulfonate bonds to metal are formed only by the less sterically hindered SO<sub>3</sub> group at the 3 position of Og. All Og O atoms that do not form bonds to metal act as hydrogen-bond acceptors, whereas none of the metal-bonding O atoms do so. Notice that, despite the presence of several potential metal complexing groups, Og does not form polymeric coordination networks with group 2 metals or Li. This is in contrast to the 1-dimensional polymeric chains and ladders found for many smaller sulfonated azo dyes with Li, Ca, and Ba.<sup>3a,3b</sup> Côté and Shimizu recently showed that the behavior of silver(I) sulfonate complexes could be understood by treating arylsulfonates as organic fragments of variable breadth pendant on SO<sub>3</sub>.<sup>11a</sup> Maximum μ<sup>6</sup> metal coordination of a sulfonate is possible only with the smallest (narrowest) organic groups. As the breadth of the organic fragment increases, SO<sub>3</sub>-M bridging behavior is replaced by rival metal-to-ligand interactions. A similar explanation based on ligand breadth and steric hindrance would be consistent both with the ligand binding series proposed above and with the reluctance of Og to form coordination polymers with Li and the group 2 metals.

**Class 3: Polymeric Coordination Complexes, Na.** Na has an electronegativity similar to those of Sr and Ba and, like them, forms bonds to both SO<sub>3</sub> and water, although the structure formed is no longer discrete. The increased metal/ligand ratio means that Na<sub>2</sub>(Og) forms a 3-dimensional coordination polymer (Figure 4), with both the sulfonate groups and the keto O atom involved in metal bonding. (In terms of networks and nodes, moving from group 2 to group 1 metals doubles the number of nodes and so promotes increased connectivity.) For Og, as for the simple para and meta azo dyes,<sup>3a</sup> the polymeric structure also propagates through metal-bridging water ligands for Na and for the heavier group 1 metals, whereas for Li and the group 2 metals, all water ligands are terminal. Some details of the sulfonates' bonding behavior are given in Table 3, but as

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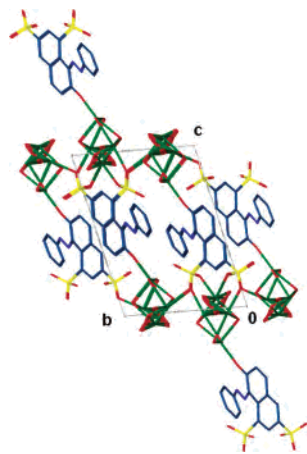


Figure 4. Extended structure of  $\text{Na}_2(\text{Og})$ .

one of the Na atoms and its dependent  $\text{H}_2\text{O}$  ligands are disordered over three sites, detailed interpretation is complicated.

In an attempt to isolate an ordered phase,  $\text{Na}_2(\text{Og})$  was recrystallized from ethanol. This gave a mixed ethanolate/hydrate,  $\text{Na}_2(\text{Og})\cdot\text{EtOH}$ , that displays several interesting features. Ethanol is both a poorer ligand than water and less inclined to act as a metal–metal bridge. As the crystallization of these metal salts can be viewed as a ligand competition reaction between the dye and the solvent, it follows that fewer metal–solvent interactions should mean more metal–**Og** bonds. For  $\text{Na}_2(\text{Og})\cdot\text{EtOH}$ , both of the  $\text{SO}_3$  groups are coordinated to metals, and the 3- $\text{SO}_3$  group attains a much higher coordination mode ( $\eta^3, \mu^5$  in the nomenclature of ref 7a) than seen elsewhere; see Table 3. Similar solvent effects on structure have been described for  $[\text{Na}][\text{O}_3\text{SC}_6\text{H}_4\text{NNC}_6\text{H}_4\text{NMe}_2]$  crystallized from water, methanol, and ethanol.<sup>3a</sup> A more subtle structural change can be seen by comparing Figures 4 and 5. The standard arrangement of these arylsulfonate complexes is alternation of organic and inorganic layers, as seen for  $\text{Na}_2(\text{Og})$ . In these structures, the individual layers are connected to each other by hydrogen-bonding and/or metal-to-dye bonds involving organic substituents other than sulfonate.  $\text{Na}_2(\text{Og})\cdot\text{EtOH}$ , however, does not use the ketone O atom to bond to Na and instead adopts a 2-dimensional network structure featuring an organic bilayer motif. There are no significant intermolecular contacts between the two organic layers, and so, each 2-dimensional coordination network is isolated from the others. Thus,

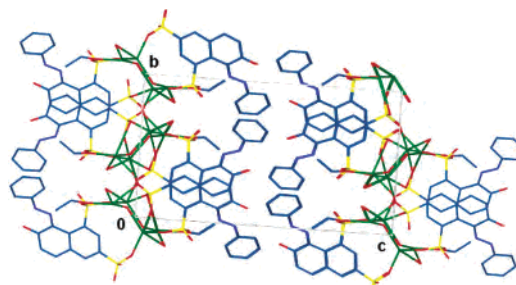


Figure 5. Extended structure of  $\text{Na}_2(\text{Og})\cdot\text{EtOH}$ .

although  $\text{Na}_2(\text{Og})\cdot\text{EtOH}$  makes more dye-to-Na bonds than  $\text{Na}_2(\text{Og})$ , it makes a lower-dimensional polymer because it does not utilize the ketone O atom to coordinate Na.

**Mixed-Metal Salts, Na/K, Na/Rb, and Na/Cs.** Preparing all of the other alkali and alkaline earth metal salts by reacting the Na dyestuff with a slight excess of the appropriate metal halide appears to have no straightforward, logical basis, but in our hands, this has worked smoothly to make many (approximately 120) pure, monosulfonated compounds. With the disulfonate **Og**, this is not the case. The heavier group 1 metals K, Rb, and Cs are isolated not as pure **Og** complexes but as mixed Na/M species. The amount of Na incorporated increases as group 1 is descended, being 0.8:1.2, 1:1, and 1.5:0.5 for Na/K, Na/Rb, and Na/Cs, respectively. Samples of  $\text{Na}_{1.5}\text{Cs}_{0.5}(\text{Og})$  were prepared using a variety of initial Na/Cs ratios from 1:1.5 to 1:7.5. All gave exactly the same ordered crystalline material. An attempt to prepare homometallic Cs(**Og**) via the free acid of Orange G failed as, in our hands, adding HCl to Na(**Og**) gave a sticky, Na-containing solid. Results from an experiment involving varying initial Na/K ratios were not as clear-cut. Differences of around 10% in K content were apparent, but the disorder present in the metal and water sites of these crystals precluded accurate analysis. Commercial colorants are often provided at relatively low purities and contaminated with “inorganic salts”. The observation of mixed metal ions within the crystal, as opposed to physical mixtures of different salts, is rarely reported<sup>12</sup> for “organic salt” species but might help to explain why purification techniques based on recrystallization are often unhelpful in the case of sulfonated dyes. The quality of both the K and Rb structures is adversely affected by disorder in the metal and  $\text{H}_2\text{O}$  positions, but it can be seen in Table 3 that both these structures and the Cs structure are of the same type as that of  $\text{Na}_2\text{Og}$ , i.e., all

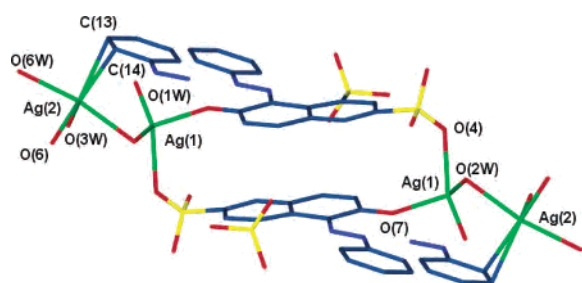
Table 3. Coordination Behavior of **Og**

metal	structural class for <b>Og</b>	coordination at 3- $\text{SO}_3$	coordination at 1- $\text{SO}_3$	coordination of ketone	total no. of M–O( <b>Og</b> ) bonds.	total no. of M–O( <b>Og</b> ) bonds per M ion	no. of bound $\text{OH}_2$ groups per M ion
Mg	1	none	none	none	0	0	6
Ca	1	none	none	none	0	0	7
Li	1	none	none	none	0	0	4
Sr	2	$\eta^1, \mu^1$	none	none	1	1	7
Ba	2	$\eta^2, \mu^2$	none	none	2	2	7
Na(EtOH)	3	$\eta^3, \mu^5$	$\eta^1, \mu^1$	none	6	3	3
Na	3	$\eta^{0or1}, \mu^{0-2}$	$\eta^{0or1}, \mu^{0-2}$	yes	3	1.5	3.33
K and Na	3	$\eta^1, \mu^1$	$\eta^1, \mu^1$	yes	3	1.5	3
Rb and Na	3	$\eta^1, \mu^1$	$\eta^1, \mu^1$	yes	3	1.5	3.25
Cs and Na	3	$\eta^2, \mu^3$	$\eta^1, \mu^1$	yes	5	2.5	3
Ag		$\eta^3, \mu^3$	none	yes	5	2.5	2

**Table 4.** Selected Geometrical Parameters for the Og Dianion and Related Dyes (Å or deg)

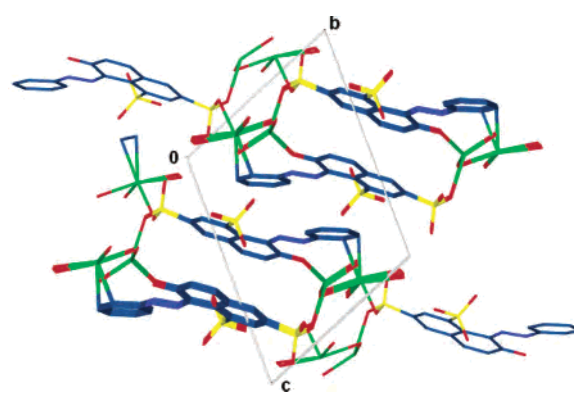
	N1=N2	N1-C8	C8-C7	C7=O7	O7...N2	1-SO <sub>3</sub> OSCC <sup>a</sup>	3-SO <sub>3</sub> OSCC <sup>a</sup>
Orange G							
Mg $\epsilon^b$	1.297(3)	1.349(3)	1.454(3)	1.273(3)	2.513(3)	-22.3(2)	-2.2(2)
Mg $\zeta^b$	1.296(3)	1.342(3)	1.453(3)	1.271(3)	2.508(3)	20.6(2)	-15.9(2)
Mg $\eta^b$	1.298(3)	1.342(3)	1.462(3)	1.269(3)	2.517(3)	-16.6(2)	<sup>c</sup>
Mg <sup>6</sup>	1.303(2)	1.339(3)	1.462(3)	1.269(3)	2.530	16.6	19.6
Li <sup>6</sup>	1.290(2)	1.341(2)	1.455(2)	1.270(2)	2.500	18.5	-0.1
Ca <sup>6</sup>	1.291(4)	1.350(5)	1.447(5)	1.262(5)	2.516	21.7	9.1
Sr	1.293(3)	1.347(4)	1.446(4)	1.277(3)	2.551(4)	-20.0(2)	27.3(2)
Ba	1.300(6)	1.334(6)	1.455(7)	1.268(7)	2.522(6)	-25.1(5)	20.6(5)
Na	1.299(3)	1.342(3)	1.452(3)	1.271(2)	2.542(3)	-22.6(2)	-24.7(2)
Na(EtOH)	1.306(2)	1.338(2)	1.465(3)	1.263(2)	2.497(2)	16.0(2)	-0.6(2)
Cs	1.300(2)	1.342(3)	1.457(3)	1.260(3)	2.533(3)	-24.6(2)	21.5(2)
Ag	1.297(4)	1.340(4)	1.458(4)	1.269(4)	2.493(4)	-11.3(3)	-9.0(3)
Related Dyes							
Ca4BCl <sup>14</sup>	1.304(2)	1.333(2)	1.458(3)	1.257(2)	2.502(2)		
JARPEX <sup>15</sup>	1.307	1.348	1.454	1.284	2.556		

<sup>a</sup> OSCC torsion angle closest to 0°. <sup>b</sup> Mg', Mg'', and Mg''' are the three independent dianions present in Mg(Og). <sup>c</sup> -4.3(3)° and 21.1(3)° for the two disordered components.

**Figure 6.** Detail of the Ag coordination in Ag<sub>2</sub>Og. Note the Ag  $\pi$  interaction.

available O-containing substituents of **Og** form bonds to metals, and this results in 3-dimensional coordination polymers. Na<sub>0.8</sub>K<sub>1.2</sub>(Og) and NaRb(Og) have near-isomorphic unit cells (Table 1). The unit cell of Na<sub>2</sub>(Og) is also related, and it is tempting to link this cell geometry to structural type, but this is not so. Note that the structurally dissimilar Ba(Og) has a unit cell that is even closer to that of Na<sub>2</sub>(Og), and indeed, with some minor manipulation, that of Sr(Og) is also related.

**Ag(I) Complex of Og.** Transition metal ions do not usually bond to arylsulfonates from aqueous solution, instead forming fully hydrated ions, but Ag(I) is an exception.<sup>11</sup> Ag<sub>2</sub>(Og) is found to form a 2-dimensional coordination polymer by using both the 3-SO<sub>3</sub> and the ketone O atom to bond to Ag. Figure 6 shows the detail of how the Ag-ketone bond is used to link the inorganic layers together, and Figure 7 shows the full polymeric structure. In this respect, Ag(I) is reminiscent of the heavier group 1 metals, but it differs from them in two ways. First, the 1-SO<sub>3</sub> group does not bond to any metal cation, and second, there is extensive and strong Ag  $\pi$  bonding involving the phenyl group of **Og**. Each Ag atom makes four Ag-O bonds in the range 2.298(2)–2.526(3) Å. These bonds involve all types of O atom. Each Ag atom also forms one longer Ag-O bond [2.836(3) and

**Figure 7.** Extended structure of Ag<sub>2</sub>Og viewed along the *a* axis.

2.956(2) Å) to a SO<sub>3</sub> group, and each completes its coordination sphere with Ag-C contacts; however, those of Ag<sub>2</sub> are much shorter than those to Ag<sub>1</sub> [compare Ag<sub>2</sub>-C13, 2.545(3); Ag<sub>2</sub>-C14, 2.562(3), and Ag<sub>1</sub>...C11, 3.328(3) Å]. These bond lengths are in line with those found for other silver(I) arylsulfonates,<sup>11a</sup> but make interesting contrasts to those found in other Ag(I) coordination polymers. In the well-developed field of silver bipyridyl derivatives,<sup>13</sup> the Ag-N<sub>pyridyl</sub> distance is consistently around 2.15 Å, whereas secondary bonding to poor ligands such as nitrate or perchlorate gives Ag-O distances of 2.65–3.15 Å, and Ag-C  $\pi$  interactions are regarded as significant at around 3.20 Å. This highlights the relative strength and importance of the Ag  $\pi$  bonds in Ag<sub>2</sub>(Og).

#### Molecular Structure and Coordination Behavior of Og.

Both the locations of the H atoms in the electron density syntheses and the pattern of long and short bonds reported in Table 4 confirm that, in the solid state, **Og** exists largely as the ketohydrazone tautomer and that an intramolecular hydrogen bond exists between the keto and hydrazone moieties. Similar tautomerism and geometric parameters are observed

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for other 2-naphthol-based colorants, whether anions<sup>14</sup> or neutral molecules.<sup>15</sup> In their work on the NH<sub>4</sub>, Li, Mg, and Ca salts of **Og**, Ojala et al. observed that the dianion was nonplanar, that the S–C bond of the 1-SO<sub>3</sub> group was always longer than that of the 3-SO<sub>3</sub> group, and that 1-SO<sub>3</sub> was displaced to the opposite face of the naphthalene rings from the azo and 3-SO<sub>3</sub> groups.<sup>6</sup> These statements are also true for the new structures described here (S–C bond ranges of 1.792–1.808 and 1.760–1.772 Å for 1-SO<sub>3</sub> and 3-SO<sub>3</sub> respectively). However, ref 6 also states that the 1-SO<sub>3</sub> groups always adopt a staggered orientation with respect to the arene whereas 3-SO<sub>3</sub> groups are eclipsed. Table 4 shows that, with the extra data now available, this no longer holds. 3-SO<sub>3</sub> groups can be either staggered or eclipsed or even disordered and hence “both”.

### Conclusions

This study highlights that the concept of structurally classifying sulfonated azo dye salts as solvent-separated ion-pairs, as “simple” complexes, or as “higher-connectivity” complexes can be extended to s-block salts of **Og**. As for monosulfonated dyes, the nature of the metal ion guides the structural type adopted, with the most electronegative metals favoring M–OH<sub>2</sub> bond formation and hence solvent-separated ion-pair structures and the most electropositive

metals forming higher-connectivity complexes with more M–O<sub>3</sub>S bond formation. However, the structural influence of the ligand is also apparent. **Og** is a poorer ligand for s-block metals than para- or meta-monosulfonated azo dyes; thus, its Li complex exists as the [Li(OH<sub>2</sub>)<sub>4</sub>] salt, and both the Sr and Ba salts form simple discrete moieties rather than the extended polymers seen elsewhere. The steric arguments presented by Côté and Shimizu, for changing coordination behavior in silver(I) arylsulfonate complexes,<sup>11a</sup> seem equally applicable to s-block salts of sulfonated azo dyes and predict well the observed metal binding series of para-monosulfonate > meta-monosulfonate > **Og**. The structure of Ag<sub>2</sub>(**Og**) has many features in common with the class 3 **Og** salts of the heavy group 1 metals, but in fact differs significantly from them by incorporating strong M–π bonds not seen elsewhere. The K, Rb, and Cs **Og** species themselves also differ from their simple monosulfonated relatives by forming as mixed-metal Na/M salts.

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**Supporting Information Available:** Crystallographic data in CIF format, tables of hydrogen-bonding interactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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