Disulfonated azo-dyes. Metal coordination and ion-pair separation in twelve *M*(II) compounds of Ponceau Xylidine and Crystal Scarlet.

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Abstract

The structures of seven divalent metal cation compounds of Ponceau Xylidine (PX) aka Acid Red 26, CI 16150, and of five divalent metal cation compounds of Crystal Scarlet (CS) aka Acid Red 44, CI 16250, are presented. In all cases the structures obtained were solvates with DMF and/or water present. The disulfonated naphthalene based azo anions adopt hydrozone tautomeric forms. The structures of the Mg salt and of four transition metal forms (M = Co, Ni, Cu and Zn) of PX are found to form an isostructural series. All have solvent-separated ion-pair (SSIP) type structures and formula $[M(OH_2)_6][PX]\cdot DMF$. The Ca salt of PX also has a SSIP structure, but has a higher hydration state, $[Ca(OH_2)_7][PX]\cdot 2.5H_2O$. In contrast, the Sr salt of PX $[Sr(PX)(DMF)_2(OH_2)_{0.5}]_n$ forms a one-dimensional coordination polymer. Both the Ca and Sr salts of CS have SSIP structures, namely $[Ca(OH_2)_7][CS]\cdot H_2O$ and $[Sr(OH_2)_8][CS]\cdot H_2O$ whilst the heavier Ba analogue $[Ba(CS)(DMF)(OH_2)_3]_n$ forms a one-dimensional coordination polymer. Unlike PX, two CS structures containing transition metals are found to be coordination complexes, $[Cu((CS)(DMF)_4]\cdot H_2O$ and $[Zn(CS)(DMF)_3(OH_2)]_n\cdot n/2\ Et_2O$. This suggests that CS is a better ligand than PX for transition metals. The Cu complex forms discrete molecules with Cu in a square pyramidal environment, whilst the Zn species is a one-dimensional coordination polymer based on octahedral Zn centres.

1. Comment

Salt selection is a well known technique in the pharmacy industry, where choosing the correct counterion for an organic pharmaceutically active ingredient (API) is a common step that allows the material properties of the API to be idealized whilst retaining most of the API's biological functionality (Stahl & Wermuth, 2008). Similar techniques are used in other industries, including the colourants industry where many so called "organic" colourants are in fact metal salts or complexes of an organic chromophore containing species (Christie & MacKay, 2008; Hao & Iqbal, 1997; Zollinger, 2003). A large and commercially important subset of such colourants are salt forms of sulfonated azo species. Such compounds are ubiquitous throughout dye and pigment chemistry, but relationships between the structures of their salt forms and the material properties of interest (*e.g.* solubility, fastness, habit and colour) are still poorly understood. This is at least partly because many such materials display highly anisotropic or otherwise sub-optimal crystal growth behaviour, which has led to a relative lack of available crystal structures. Reasonable amounts of structural data are available for some relatively small, monosulfonated, monoazo species with C_6 aromatic rings, such as the one shown in the scheme. This is largely because these simpler species are more soluble and have better crystal growth properties (Kennedy *et al.*, 2001; Kennedy *et al.*, 2004; Kennedy *et al.*, 2009). However, crystal structures of larger naphthalene-based, or more functionalized, sulfonated azo dyes and especially pigments are still relatively rare (Kennedy *et al.*, 2012; Ojala *et al.*, 1994*a*; Kennedy *et al.*, 2006). Many of the structures that are known have only been accessed through use of "special" techniques such as structure solution from powder diffraction or electron diffraction or through utilization of synchrotron techniques (Beko *et al.*, 2012; Schmidt *et al.*, 2009; Gorelik *et al.*, 2009; Kennedy *et al.*, 2000; Ivashevskaya *et al.*, 2009; Grzesiak-Nowak *et al.*, 2019). Almost all available structures of commercially relevant sulfonated azo anions are of s-

block metal salt forms, especially Ca, rather than of transition metal complexes.

Here we present structures of both alkaline earth metal salts and of first row transition metal complexes of two naphthalene based disulfonated azo dyes, Ponceau Xylidine aka Acid Red 26, CI 16150, and Crystal Scarlet aka Crystal Ponceau 6R or Acid Red 44, CI 16250. Both dyes have been used as biological stains and Crystal Scarlet has been used as a food colourant, as a textile dye and in cosmetics. The structures presented herein that contain the Ponceau Xylidine dianion (PX) are $[Mg(OH_2)_6][PX] \cdot DMF$ (I), $[Ca(OH_2)_7][PX] \cdot 2.5H_2O$ (II), $[Sr(PX)(DMF)_2(OH_2)_{0.5}]_n$ (III) and the transition metal series $[M(OH_2)_6][PX] \cdot DMF$ where M = Co (IV), Ni (V), Cu (VI) and Zn (VII). The structures presented herein that contain the Crystal Scarlet dianion (CS) are $[Ca(OH_2)_7][CS] \cdot H_2O$ (VIII), $[Sr(OH_2)_8][CS] \cdot H_2O$ (IX), $[Ba(CS)(DMF)(OH_2)_3]_n$ (X), $[Cu((CS)(DMF)_4] \cdot H_2O$ (XI) and $[Zn(CS)(DMF)_3(OH_2)]_n \cdot n/2$ Et$_2$O (XII).

Section 1.1. Metal Coordination in Compounds of PX.

Previous studies on s-block metal salts of simple mono-sulfonated azo dyes and on the disulfonate Orange G, showed that when crystallized from aqueous solution the less electropositive metal ions formed solvent-separated ion-pair (SSIP) species with no direct bonding between the metal ion and the sulfonate groups of the azo species (Ojala *et al.*, 1994*b*; Kennedy *et al.*, 2004; Kennedy *et al.*, 2006). More electropositive metal ions formed complexes with direct metal to sulfonate bonds. Exactly which metal ions made SSIPs, and which formed M–O$_3$S bonds, was found to depend on the nature of the azo anion. For *para*-sulfonated azo dyes only Mg formed SSIP species, for *meta*-sulfonated azo dyes both Mg and Ca were found to form SSIP structures whilst for Orange G the Mg, Ca and Li structures were all SSIP in nature. This suggests a ligand strength order of *para*-sulfonated > *meta*-sulfonated > Orange G. Similar observations with regards to metal ion elecronegativity and the occurance of SSIP structures were made for more complicated sulfonated azo dyes and pigments crstallized from water and/or DMF (Kennedy *et al.*, 2004; Kennedy *et al.*, 2012).

Structure (I) is a DMF solvate of the Mg salt of PX. As expected from the work cited above it is a SSIP structure featuring a hexaaquamagnesium cation that interacts with the PX anion only through hydrogen bonding (Figure 1). The structure also contains a disordered DMF solvent molecule. A major structural feature is that all three structural components, the cations, anions and solvents lie on crystallographic mirror planes, thus Z' = 0.5. For the cation, the plane runs through Mg1, O1W and O3W. For the mostly planar anion and DMF all atoms lie on the mirror plane - with the exception of the non-coplanar O atoms of the sulfonate groups and the H atoms of methyl groups.

The Ca salt of PX, (II), was also found to be a SSIP structure, though with a $[Ca(OH_2)_7]$ cation rather than the hexaaqua cation found for (I), see Fig 2. This behaviour is not uncommon, as Ca often forms SSIP species with sulfonated azo dyes (Kennedy *et al.*, 2004; Ojala *et al.*, 1994*b*), although with pigment species coordination bond formation is perhaps more commonly observed (Ivashevskaya *et al.*, 2009; Kennedy *et al.*, 2012). Again in line with literature suggestions, moving to the more electropositive metal Sr gives a structure with coordination of metal to sulfonate. This structure is the Z' =2 structure (III). Its asymmetric unit contains two 8-coordinate Sr centres, two PX anions, 4 coordinated DMF molecules and a single coordinated water molecule. Two of the DMF ligands and the water ligand are disordered. The contents of the asymmetric unit are shown in Fig 3 whilst the full coordination geometry of each Sr centre can be seen in Fig 4. A l1 four independent sulfonate groups form bonds to Sr centres. The sulfonate groups *meta* to the azo groups each form O–Sr bonds with two of their O atoms, each of these are supported by an additional chelating O–Sr bond supplied by the azo ligand's C=O group. These O–Sr bonds link Sr1 and Sr2 into dimeric units, supported by a single Sr—O—Sr bridge involving a DMF ligand. At the other end of the naphthalene units, the sulfonate groups remote from the azo groups each form only one O–Sr bond. This is enough to give the broken ladder structure shown in Figure 4. It is a one-dimensional coordination polymer that propagates parallel to the crystallographic c direction.

The solid-state coordination behaviour of sulfonated azo dye anions with transition metal cations is less well studied than with s-block metal cations. In general SSIP structures are favoured with no M to sulfonate bonding (Kennedy *et al.*, 2010; Oh *et al.*, 2017). Given the trends discussed above, this is perhaps unsurprizing as bond formation is associated with more electropositive rather than less electropositive metals. This is also a reflection of a wider trend where sulfonated aryl anions in general do not normally form bonds to transition metal cations, at least not when polar solvents are available as competitor ligands (Cote & Shimizu, 2003). However there are exceptions. Ag(I) does form coordination bonds with sulfonated azo dyes (Dodds *et al.*, 2017; Kennedy *et al.*, 2006) and first row transition metal cations are known to bond to sulfonated azo dye species, especially when the dye molecule has other potentially metal binding groups available to support the M to SO_3 contacts (Chen *et al.*, 2013; Mahmudov *et al.*, 2015; Lu *et al.*, 2009). Crystallization of PX in the presence of Co(II), Ni(II), Cu(II) and Zn(II) gave a series of SSIP structures (IV) to (VII) that were all isomorphous and isostructural both with each other and also with the Mg structure (I), Figure 5. A l l structural features (such as the disordered nature of the DMF solvent) are identical throughout. Such an isostructural series is relatively rare and may potentially be useful in future structure-property investigations. Examining the unit-cell dimensions, we could find no obvious simple relationship between any of, ionic radius, M–O bond lengths, cell volume and/or cell lengths.

Section 1.2. Metal Coordination in Compounds of CS.

As can be seen from Scheme 1, CS differs from PX in two main ways. On the polar side of the azo bond, the sulfonate groups are placed differently, and on the non-polar side of the azo bond a naphthyl group has replaced the smaller xylyl group of PX. CS differs from the previously studied dye Orange G only in that CS has a large naphthyl group in place of Orange G's smaller phenyl group.

In common with PX, the Ca salt of CS is found to be a SSIP structure with a heptaaqua calcium cation, namely $[Ca(OH_2)_7][CS]·H_2O$ (VIII). This structure has four crystallographically independent cation-anion-solvent units per asymmetric unit, $Z' = 4$, but is otherwise unremarkable in terms of its metal to ligand bonding, Fig. 6. What is interesting is that the Sr salt of CS is also found to be a SSIP structure, $[Sr(OH_2)_8][CS]·H_2O$ (IX), Fig. 7. This is in contrast to the one-dimensional-coordination polymer structure of the Sr salt form of PX (III) and also contrasts with the literature (Kennedy *et al.*, 2006; Kennedy *et al.*, 2012). No other sulfonated azo colourant is known to form a SSIP structure where Sr bonds to only water, or indeed to any other solvent. This suggests that CS is a poorer/weaker ligand for s-block metal ions than the other sulfonated azo colourants that have been studied. As the only difference between CS and Orange G is naphthyl *versus* phenyl groups, this difference in coordination behaviour could be related to the large non-polar volume of the CS ion.

As with other Ba salts of sulfonated azo dyes and pigments, CS does form a coordination complex with Ba. The resulting structure is $[Ba(CS)(DMF)(OH_2)_3]_n$ (X), Fig. 8. The Ba centre is 8 coordinate and forms bonds to 3 terminal water ligands and a terminal DMF ligand as well as to four Ba—O bonds with O atoms from the anion's sulfonate groups. The SO_3 group *syn* to the azo bond forms only one Ba—O bond, but the SO_3 group remote from the azo forms three Ba—O bonds using all 3 of its O atoms. This contrasts to PX, where the SO_3 group closest to the azo group is the preferred metal coordination site. This difference will be due to the sterically hindered *syn* SO_3 site in CS and its location away from the potentially chelating and/or supporting C=O group. The Ba centres are linked through Ba—O—S—O—Ba interactions involving the remote SO_3 group. The resulting one-dimensional-coordination polymer is further supported by the coordination bond involving the other SO_3 group and by hydrogen bonding. The polymer propagates parallel to the crystallographic b direction, see Fig. 9.

Two transition metal complexes of CS were also prepared and structurally characterized. These are [Cu((CS)(DMF)$_4$]·H$_2$O (XI) and [Zn(CS)(DMF)$_3$(OH$_2$)]$_n$.n/2 Et$_2$O (XII), Figs. 10 and 11. That both of these species are complexes with *M* to sulfonate bonds contrasts to the behaviour of PX and to the bulk of the literature on transition metal behaviour with sulfonated aryl species (Cote & Shimizu, 2003). It also means that curiously CS seems to be a better ligand for transition metal ions than PX, but a worse ligand for s-block metals ions than PX. Note that PX is the species that behaves in the same structural way as most other literature sulfonated azo species and so it is the behaviour of CS that is somewhat abnormal. The Cu(II) complex (XI) forms a discrete molecule with a square pyramidal Cu centre. The four DMF ligands form the base of the pyramid. The apical bond is a single Cu—O bond involving the SO$_3$ group *syn* to the azo group. This latter interaction is considerably longer (2.173 (3) Å) than the four Cu—O bonds involving DMF ligands (1.944 (3) to 1.955 (3) Å). The plane of the azo ligand is approximately parallel to the CuO$_4$ (O from DMF) coordination plane. The Zn(II) complex (XII) has an octahedral Zn centre with *trans* sulfonate groups and *mer* DMF ligands. Both of the sulfonate groups make a single Zn—O bond. In contrast to the Cu complex, the bonds involving SO$_3$ are of similar length to the bonds involving solvent ligands (compare 2.096 (4) and 2.101 (4) Å with 2.052 (4) to 2.132 (4) Å). Each azo ligand bonds to two Zn centres, with the result that this structure is a one-dimensional-coordination polymer that propagates parallel to the crystallographic c direction, see Fig. 12. As in (XI), the plane of the azo ligand is approximately parallel to the ZnO$_4$ (O from solvent) coordination plane.

Section 1.3. Geometry of the Anions PX and CS

In all structures (I) to (XII), the anions are found to exist as the hydrozone tautomers, with a protonated N atom rather than an OH group. The N—H acts as an intramolecular hydrogen bond donor to the ketone group, giving a 6-membered ring motif. This is in line with prior literature where all naphthol fragments with similar geometries exist as hydrozone tautomers (Kennedy *et al.*, 2000; Kennedy *et al.*, 2006; Kennedy *et al.*, 2012) but phenol fragments always exist as the alternative hydroxy-azo tautomer (Kennedy *et al.*, 2004; Kennedy *et al.*, 2009). Tables 14 and 15 show that both PX and CS give the expected pattern of alternating bond shortening and lengthening that would be expected for hydrozone tautomers as opposed to hydroxy-azo tautomers. Note that the largest distortions in bond length are not for the NN bond. For PX the NN bond is approximately 0.02 Å longer than the bonds found in a relevant hydroxy-azo tautomer and 0.05 Å longer than would be expected for a "pure" azo species with no OH group (Kennedy *et al.*, 2001). The C—N, C—C and C—O distances consistently change by larger amounts (approximately 0.04 to 0.07 Å). A similar pattern is observed for the CS anions, which show slightly larger average changes than for PX. For the isostructural structures (I) and (IV) through to (VII) the PX azo anion is constrained to be planar by the crystallographic m symmetry. In structures (II) and (III) the PX anion is also very planar (maximum value for the C2C1C11C12 or equivalent torsion angle is 2.8 (2) °) a structural feature presumably aided by the intramolecular hydrogen bond. The CS anions show somewhat more deviation from planarity. This is partly seen in slightly larger twists about the NN bond (equivalent torsions up to 6.9 (2) °) but is also apparent in the sulfonate groups *syn* to the azo groups. These are forced out of the plane of their parent aromatic rings, presumabley due to steric effects.

Section 1.1. Packing

Simple sulfonated azo dyes approximate stepped linear spacers with the hydrophillic SO$_3$ group at one end (the "head") and usually another hydrophillic substituent at the opposite "tail" end. As such, the typical packing motif found in the literature for their salts forms is a simple layered structure where layers of azo anions lie between layers of cations (and solvent molecules when present) with the hydrophillic head and tail groups of the azo anions linking the cation layers above and below (Kennedy *et al.*, 2004). An exception is where the SO$_3$ group is *ortho* to the azo group. Here the hydrophillic SO$_3$ group is tucked into the body of the organic molecule, and the anion loses its linear spacer geometry. It has been shown that *ortho* sulfonated azo dyes that retain their normal planar conformation do not adopt simple layered packing

modes, instead they form structures with organic bilayers. Retaining simple layering requires the anions to change to an otherwise energetically disfavoured twisted conformation (38 to 48 ° angles between the planes of the aromatic rings) (Kennedy *et al.*, 2009).

The compounds (I) to (XII) all have coplanar conformations but have hydrophillic groups only on one side of the azo bond, thus they do not obviously fit the simple description of a linear spacer with hydrophillic head and tail groups on either side of the azo group. A packing diagram of the PX salt (I) is given as Figure 13. This is clearly a simple layered structure with layers of anions and layers of cations with solvent alternating along the *c* axis. Here the azo anion is orientated so that the length of the azo bond describes a vector within its *ab* layer rather than stretching between the cation layers. As PX has a SO_3 group at either end of its naphthol group, the separation of hydrophillic substituents is great enough for it to act as a spacer in this direction instead of through the length ofthe azo as previously described. Isostructural compounds (I) and (IV) to (VII) obviously adopt the same motif but so do the other two PX structures (II) and (III), with layers extending parallel to *ab* and to *ac* respectively.

The SO_3 groups of CS are *meta* to each other and thus much closer in space than in PX. This restriction appears to preclude this anion from linking between cation layers. For the three s-block metal salts of CS, (VIII) to (X), the result is bilayer structures with layering parallel to the *ab* plane. In each organic bilayer, half of the azo anions present both their SO_3 groups to the cation layer above and half to the cation layer below. This is illustrated in Figure 14. With their direct metal to sulfonate bonds, the transition metal complexes (XI) and (XII) seem to present further geometrical restrictions. Despite being datively bonded together, for (XI) the planar azo anions and the planar $Cu(DMF)_4$ units form separate layers parallel to *ac*. However, here the plane of the azo anion lies coplanar to the plane of the layer, thus unlike the PX structures the SO_3 groups are not linking between cation layers. For (XII) the naphthyl groups form organic bilayers parallel to *bc*, Figure 15. These layers also incorporate the ether solvate molecules, but do not include the SO_3 substituted aromatic groups of the azo anion.

2. Synthesis and crystallization

With the exception of (III), all *M*(II) complexes were first prepared by adding a slight excess of MCl_2 to aqueous solutions of the Na salts of PX or CS. The *M*(II) complexes quickly precipitated and were isolated by filtration. Crystals of (I) and (X) were prepared by recrystallization from warm DMF. Crystals of (II), (VIII) and (IX) were prepared by recrystallization from warm water. Crystals of all transition metal species were prepared by vapour diffusion of diethyl ether into DMF solutions of the appropriate dye complex. Crystals of (III) were prepared by layering a DMF solution of the Na salt of PX onto an aqueous solution of $Sr(OH)_2$.

3. Refinement

Diffraction measurements on compounds (I) to (X) were carried out by the UK National Crystallography Service (Cole & Gale, 2012). For all structures, H atoms bound to C atoms were placed in the expected geometric positions and treated in riding modes with $U(H)_{iso} = 1.2U(C)_{eq}$. For aromatic groups C–H = 0.95 Å and for CH_2 groups C–H = 0.95 Å. All H atoms bound to N were refined freely and isotropically.

Table 1

Experimental details

	(I)	(II)	(III)	(IV)	(V)
Crystal data					
Chemical formula	$C_{21}H_{33}MgN_3O_{14}S_2$	$C_{18}H_{33}CaN_2O_{16.50}S_2$	$C_{24}H_{29}N_4O_{9.50}S_2Sr$	$C_{21}H_{33}CoN_3O_{14}S_2$	$C_{21}H_{33}N_3NiO_{14}S_2$

M_r	639.93	645.66	677.25	674.55	674.33
Crystal system, space group	Monoclinic, $I2/m$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $I2/m$	Monoclinic, $I2/m$
Temperature (K)	100	100	100	100	100
a, b, c (Å)	13.7743 (8), 6.8224 (4), 31.094 (2)	8.1180 (1), 12.5594 (2), 15.2110 (3)	13.0262 (4), 29.3121 (10), 14.9087 (6)	13.7311 (5), 6.8328 (3), 31.0201 (14)	13.7212 (15), 6.7937 (7), 31.012 (4)
α, β, γ (°)	90, 97.287 (5), 90	108.352 (1), 103.149 (2), 94.477 (1)	90, 97.650 (3), 90	90, 97.021 (4), 90	90, 97.144 (11), 90
V (Å^3)	2898.4 (3)	1414.48 (4)	5641.9 (3)	2888.5 (2)	2868.4 (6)
Z	4	2	8	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.28	0.45	2.12	0.81	0.89
Crystal size (mm)	$0.23 \times 0.04 \times 0.02$	$0.14 \times 0.06 \times 0.02$	$0.28 \times 0.02 \times 0.01$	$0.10 \times 0.01 \times 0.01$	$0.08 \times 0.02 \times 0.01$
Data collection					
Diffractometer	Rigaku AFC12	Enhance source with dtrek gonio	Rigaku HG Saturn724	XtaLAB AFC12	Enhance dtrek
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.39.9g (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.39.9g (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.466, 1.000	0.869, 1.000	0.671, 1.000	0.726, 1.000	0.671, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9999, 3593, 2796	49956, 6481, 5819	60839, 12896, 7917	33372, 3576, 3299	4178, 4178, 2577
R_{int}	0.058	0.029	0.094	0.040	0
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649	0.649	0.649	0.649	0.595
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.137, 1.06	0.050, 0.136, 1.04	0.064, 0.153, 1.02	0.035, 0.081, 1.07	0.090, 0.214, 1.07
No. of reflections	3593	6481	12896	3576	4178
No. of parameters	290	462	790	291	292
No. of restraints	49	79	88	48	49
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 2.1664P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0704P)^2 + 1.6221P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 11.1037P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 5.2279P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 44.5931P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.77, −0.61	0.99, −0.62	1.15, −0.61	0.62, −0.46	0.63, −0.64

	(VI)	(VII)	(VIII)	(IX)	(X)
Crystal data					
Chemical formula	$C_{21}H_{33}CuN_3O_{14}S_2$	$C_{21}H_{33}N_3O_{14}S_2Zn$	$C_{20}H_{28}CaN_2O_{15}S_2$	$C_{20}H_{30}N_2O_{16}S_2Sr$	$C_{23}H_{25}BaN_3O_{11}S_2$
M_r	679.16	680.99	640.64	706.20	720.92
Crystal system, space group	Monoclinic, $I2/m$	Monoclinic, $I2/m$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Temperature (K)	100	100	100	100	100
a, b, c (Å)	13.7392 (8), 6.7872 (3), 30.9083 (18)	13.7509 (13), 6.7836 (5), 30.931 (2)	10.0215 (2), 19.4196 (5), 28.3709 (6)	9.9942 (3), 10.1007 (4), 14.9663 (5)	7.1967 (1), 9.0311 (1), 40.7043 (4)
α, β, γ (°)	90, 97.008 (5), 90	90, 97.095 (8), 90	82.529 (2), 83.005 (2), 76.190 (2)	100.568 (3), 94.863 (2), 112.346 (3)	90, 94.615 (1), 90
V (Å^3)	2860.7 (3)	2863.2 (4)	5292.6 (2)	1353.69 (9)	2636.96 (5)
Z	4	4	8	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.98	1.08	0.47	2.23	1.73
Crystal size (mm)	0.06 × 0.01 × 0.01	0.07 × 0.01 × 0.01	0.28 × 0.07 × 0.01	0.09 × 0.02 × 0.01	0.12 × 0.05 × 0.04
Data collection					
Diffractometer	XtaLab AFC12	Enhance dtrek	Rigaku AFC12	Rigaku AFC12	Rigaku AFC12
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.39.9g (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.39.9g (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.514, 1.000	0.511, 1.000	0.789, 1.000	0.724, 1.000	0.840, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13907, 3384, 2481	12569, 2758, 1634	113814, 23071, 14733	46475, 6203, 5294	64337, 6037, 5889
R_{int}	0.079	0.125	0.062	0.077	0.020
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.639	0.595	0.639	0.649	0.649
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.079, 0.195, 1.12	0.061, 0.143, 1.03	0.060, 0.167, 1.03	0.036, 0.088, 1.02	0.020, 0.052, 1.29
No. of reflections	3384	2758	23071	6203	6037
No. of parameters	290	290	1643	417	385
No. of restraints	49	60	96	29	9
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0946P)^2 + 4.2727P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 2.7249P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2 + 4.7554P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 1.3562P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0177P)^2 + 3.3023P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.27, −0.67	0.58, −0.68	0.75, −0.69	0.57, −0.55	0.66, −0.40

	(XI)	(XII)
Crystal data		
Chemical formula	$C_{32}H_{42}CuN_6O_{12}S_2$	$C_{31}H_{40}N_5O_{11.50}S_2Zn$
M_r	830.37	796.17
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$
Temperature (K)	153	123
a, b, c (Å)	12.9973 (5), 13.6151 (7), 20.9781 (8)	44.082 (3), 9.0229 (6), 18.185 (2)
α, β, γ (°)	90, 102.875 (4), 90	90, 100.906 (9), 90
V (Å^3)	3618.9 (3)	7102.4 (11)
Z	4	8
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.79	2.64
Crystal size (mm)	$0.40 \times 0.26 \times 0.09$	$0.5 \times 0.2 \times 0.02$
Data collection		
Diffractometer	Oxford Diffraction Xcalibur E	Oxford Diffraction Gemini S
Absorption correction	Multi-scan	Analytical
	CrysAlis PRO, Oxford Diffraction Ltd., Version 1.171.34.40 (release 27-08-2010 CrysAlis171 .NET) (compiled Aug 27 2010,11:50:40) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	*CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.430, 1.000	0.520, 0.927
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17740, 7427, 5303	12833, 6492, 4529
R_{int}	0.075	0.064
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.628	0.607
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.074, 0.216, 1.05	0.071, 0.198, 1.05
No. of reflections	7427	6492
No. of parameters	500	497
No. of restraints	6	38
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.117P)^2 + 1.8738P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0897P)^2 + 12.0184P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.87, −1.22	1.33, −0.65

Computer programs: *CrysAlis PRO* (Agilent, 2014), *CrystalClear* (Rigaku, 2015), *CrysAlis PRO*, *CrystalClear*, *SIR92* (Altomare *et al.*, 1994), Atom coordinates from isostructural Co structure, *SHELXS* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) & *ORTEP-3* (Farrugia, 2012), *SHELXL2014*, *SHELXL*.

Table 2

Hydrogen-bond geometry (Å, º)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2W—H2$W\cdots$O1^{i}	0.86 (1)	1.95 (1)	2.781 (2)	164 (3)
O2W—H3$W\cdots$O1S	0.86 (1)	1.89 (4)	2.75 (4)	174 (4)
O2W—H3$W\cdots$O1S^{ii}	0.86 (1)	1.81 (3)	2.67 (3)	174 (4)
O2W—H3$W\cdots$O2S	0.86 (1)	1.92 (4)	2.77 (3)	170 (3)
O2W—H3$W\cdots$O2S^{ii}	0.86 (1)	1.65 (4)	2.51 (4)	172 (4)
O1W—H1$W\cdots$O1^{iii}	0.87 (1)	1.91 (1)	2.774 (2)	173 (3)
O4W—H5$W\cdots$O2^{iv}	0.87 (1)	1.93 (1)	2.796 (2)	171 (2)
O4W—H6$W\cdots$O3^{v}	0.88 (1)	1.88 (1)	2.757 (2)	175 (2)
O3W—H4$W\cdots$O4^{v}	0.88 (1)	1.88 (1)	2.757 (2)	176 (2)
N2—H1$N\cdots$O5	0.90 (1)	1.85 (3)	2.530 (3)	131 (3)

Symmetry codes: (i) $-x+3/2, -y+1/2, -z+1/2$; (ii) $x, -y+1, z$; (iii) $x+1/2, y-1/2, z+1/2$; (iv) $x+1/2, y+1/2, z+1/2$; (v) $-x+1/2, -y+1/2, -z+1/2$.

Table 3

Hydrogen-bond geometry (Å, º)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$W\cdots$O6^{i}	0.87 (1)	2.23 (2)	2.963 (3)	141 (3)
O1W—H1$W\cdots$O7^{i}	0.87 (1)	2.49 (3)	3.181 (3)	137 (3)
O1W—H2$W\cdots$O1	0.87 (1)	1.86 (2)	2.668 (11)	152 (4)
O1W—H2$W\cdots$O1A	0.87 (1)	2.19 (2)	3.006 (8)	156 (4)
O2W—H4$W\cdots$O6^{i}	0.89 (1)	2.03 (2)	2.862 (4)	155 (3)
O2AW—H3$AW\cdots$O2AW^{ii}	0.88 (1)	1.87 (9)	2.54 (2)	131 (10)
O3W—H6$W\cdots$O5^{i}	0.88 (1)	2.16 (4)	2.885 (4)	139 (5)
O3W—H6$W\cdots$O6^{i}	0.88 (1)	2.62 (4)	3.380 (4)	144 (5)
O3AW—H5$AW\cdots$O3AW^{iii}	0.88 (1)	1.38 (8)	2.11 (3)	137 (11)
O3AW—H5$AW\cdots$O11W^{iv}	0.88 (1)	2.65 (9)	3.269 (13)	128 (9)
O3AW—H6$AW\cdots$O5^{i}	0.88 (1)	1.82 (2)	2.700 (11)	173 (14)
O4W—H7$W\cdots$O4^{v}	0.87 (1)	2.03 (1)	2.872 (3)	162 (3)
O4W—H7$W\cdots$O6^{v}	0.87 (1)	2.65 (2)	3.325 (2)	135 (2)
O4W—H8$W\cdots$O8W	0.87 (1)	1.83 (1)	2.697 (3)	172 (3)
O5W—H9$W\cdots$O3^{vi}	0.87 (1)	1.86 (1)	2.693 (6)	161 (2)
O5W—H9$W\cdots$O3A^{vi}	0.87 (1)	1.91 (1)	2.769 (5)	171 (3)
O5W—H10$W\cdots$O5^{vii}	0.87 (1)	1.89 (1)	2.757 (2)	170 (3)
O6W—H11$W\cdots$O2^{viii}	0.87 (1)	1.95 (2)	2.812 (10)	172 (4)
O6W—H11$W\cdots$O2A^{viii}	0.87 (1)	1.84 (1)	2.711 (8)	174 (3)
O6W—H12$W\cdots$O4^{v}	0.87 (1)	1.94 (1)	2.771 (2)	160 (3)
O7W—H13$W\cdots$O1^{vi}	0.88 (1)	2.22 (2)	3.071 (13)	163 (3)
O7W—H13$W\cdots$O3^{vi}	0.88 (1)	2.43 (2)	3.108 (7)	134 (2)
O7W—H13$W\cdots$O1A^{vi}	0.88 (1)	2.07 (2)	2.937 (10)	171 (3)
O7W—H14$W\cdots$O1	0.87 (1)	2.38 (3)	2.873 (13)	116 (3)
O7W—H14$W\cdots$O9W	0.87 (1)	1.88 (2)	2.664 (4)	148 (3)
O7W—H14$W\cdots$O1A	0.87 (1)	2.63 (3)	3.177 (9)	121 (3)
O8W—H15$W\cdots$O10W^{iv}	0.90 (1)	2.34 (4)	2.846 (4)	116 (3)
O8W—H15$W\cdots$O11W^{iv}	0.90 (1)	1.90 (3)	2.569 (9)	130 (3)
O8W—H16$W\cdots$O7^{vii}	0.89 (1)	1.98 (2)	2.822 (3)	157 (4)
O9W—H17$W\cdots$O2	0.88 (1)	1.66 (2)	2.474 (10)	154 (5)
O9W—H18$W\cdots$O2^{viii}	0.87 (1)	1.93 (3)	2.733 (10)	151 (5)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O10W—H19W⋯O9W	0.88 (1)	1.84 (1)	2.706 (5)	169 (4)
O10W—H20W⋯O2W[viii]	0.88 (1)	1.93 (2)	2.740 (6)	153 (3)
O11W—H21W⋯O5W[vi]	0.89 (1)	2.18 (6)	2.808 (8)	127 (6)
N2—H1N⋯O7	0.82 (3)	1.86 (3)	2.542 (2)	140 (3)

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x+1, −y+1, −z; (iii) −x, −y+1, −z; (iv) x, y+1, z; (v) x, y, z−1; (vi) −x, −y, −z; (vii) x−1, y, z−1; (viii) −x+1, −y, −z.

Table 4
Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1W⋯O13[i]	0.88 (1)	1.99 (2)	2.802 (13)	152 (2)
O2W—H1W⋯O13[i]	0.90 (2)	1.99 (2)	2.850 (13)	160 (2)
N2—H1N⋯O7	0.87 (6)	1.89 (6)	2.575 (5)	135 (5)
N4—H2N⋯O14	0.83 (6)	1.92 (6)	2.566 (6)	134 (5)

Symmetry code: (i) −x+1, y+1/2, −z+3/2.

Table 5
Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2W—H2W⋯O1[i]	0.86 (1)	1.91 (1)	2.7623 (18)	171 (3)
O2W—H3W⋯O1S	0.86 (1)	1.82 (4)	2.67 (4)	170 (4)
O2W—H3W⋯O2S	0.86 (1)	1.89 (3)	2.74 (3)	169 (3)
O2W—H3W⋯O2S[ii]	0.86 (1)	1.65 (3)	2.51 (3)	172 (4)
O1W—H1W⋯O1[iii]	0.87 (1)	1.88 (1)	2.7415 (18)	172 (3)
O4W—H5W⋯O2[iv]	0.87 (1)	1.93 (1)	2.7903 (17)	171 (2)
O4W—H6W⋯O3[v]	0.87 (1)	1.89 (1)	2.7532 (17)	172 (2)
O3W—H4W⋯O4[v]	0.87 (1)	1.88 (1)	2.7453 (17)	178 (2)
N2—H1N⋯O5	0.87 (3)	1.79 (3)	2.533 (3)	142 (3)

Symmetry codes: (i) −x+3/2, −y+1/2, −z+1/2; (ii) x, −y+1, z; (iii) x+1/2, y−1/2, z+1/2; (iv) x+1/2, y+1/2, z+1/2; (v) −x+1/2, −y+1/2, −z+1/2.

Table 6
Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2W—H2W⋯O1[i]	0.88 (1)	1.95 (5)	2.767 (9)	154 (11)
O2W—H3W⋯O1S	0.88 (1)	1.85 (7)	2.72 (6)	169 (11)
O2W—H3W⋯O2S	0.88 (1)	1.91 (6)	2.77 (5)	165 (9)
O2W—H3W⋯O2S[ii]	0.88 (1)	1.51 (5)	2.37 (4)	168 (12)
O1W—H1W⋯O1[iii]	0.88 (1)	1.88 (3)	2.743 (8)	166 (10)
O4W—H5W⋯O2[iv]	0.88 (1)	1.92 (2)	2.793 (7)	172 (6)
O4W—H6W⋯O3[v]	0.88 (1)	1.89 (2)	2.758 (7)	169 (7)
O3W—H4W⋯O4[v]	0.88 (1)	1.87 (2)	2.747 (7)	174 (8)
N2—H1N⋯O5	0.90 (1)	1.77 (6)	2.556 (13)	145 (9)

Symmetry codes: (i) −x+3/2, −y+1/2, −z+1/2; (ii) x, −y+1, z; (iii) x+1/2, y−1/2, z+1/2; (iv) x+1/2, y+1/2, z+1/2; (v) −x+1/2, −y+1/2, −z+1/2.

Table 7

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O2W—H2W···O1^i	0.88 (1)	1.99 (4)	2.780 (6)	149 (6)
O2W—H3W···O1S	0.88 (1)	2.41 (7)	2.91 (3)	116 (6)
O2W—H3W···O2S	0.88 (1)	2.16 (7)	2.71 (3)	120 (6)
O2W—H3W···O2S^{ii}	0.88 (1)	1.89 (8)	2.31 (3)	108 (6)
O1W—H1W···O1^{iii}	0.88 (1)	1.88 (1)	2.749 (5)	171 (6)
O4W—H5W···O2^{iv}	0.88 (1)	1.92 (2)	2.786 (5)	167 (5)
O4W—H6W···O3^v	0.88 (1)	1.89 (2)	2.758 (5)	171 (5)
O3W—H4W···O4^v	0.88 (1)	1.86 (2)	2.723 (5)	170 (6)
N2—H1N···O5	0.90 (1)	1.81 (5)	2.536 (7)	137 (6)

Symmetry codes: (i) −x+3/2, −y+1/2, −z+1/2; (ii) x, −y+1, z; (iii) x+1/2, y−1/2, z+1/2; (iv) x+1/2, y+1/2, z+1/2; (v) −x+1/2, −y+1/2, −z+1/2.

Table 8

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O2W—H2W···O1^i	0.88 (1)	1.90 (2)	2.760 (6)	167 (7)
O2W—H3W···O1S	0.87 (1)	2.11 (4)	2.95 (3)	161 (8)
O2W—H3W···O2S	0.87 (1)	1.90 (5)	2.73 (3)	159 (8)
O2W—H3W···O2S^{ii}	0.87 (1)	1.61 (5)	2.41 (4)	150 (8)
O1W—H1W···O1^{iii}	0.88 (1)	1.89 (1)	2.761 (5)	174 (6)
O4W—H5W···O2^{iv}	0.88 (1)	1.91 (1)	2.781 (5)	173 (4)
O4W—H6W···O3^v	0.88 (1)	1.92 (2)	2.761 (5)	161 (4)
O3W—H4W···O4^v	0.88 (1)	1.85 (1)	2.724 (5)	172 (5)
N2—H1N···O5	0.98 (8)	1.73 (8)	2.535 (8)	137 (7)

Symmetry codes: (i) −x+3/2, −y+1/2, −z+1/2; (ii) x, −y+1, z; (iii) x+1/2, y−1/2, z+1/2; (iv) x+1/2, y+1/2, z+1/2; (v) −x+1/2, −y+1/2, −z+1/2.

Table 9

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O18	0.88 (1)	2.08 (1)	2.913 (3)	157 (3)
O1W—H2W···O8^i	0.87 (1)	1.86 (1)	2.733 (3)	175 (4)
O2W—H3W···O32W	0.87 (1)	1.96 (1)	2.830 (3)	178 (3)
O2W—H4W···O21^{ii}	0.87 (1)	1.92 (2)	2.751 (3)	161 (3)
O3W—H5W···O10	0.88 (1)	1.94 (1)	2.809 (3)	174 (3)
O3W—H6W···O20	0.88 (1)	1.96 (1)	2.813 (3)	164 (3)
O4W—H7W···O27^{iii}	0.88 (1)	1.84 (1)	2.693 (3)	164 (3)
O4W—H8W···O17W	0.87 (1)	2.13 (2)	2.861 (4)	141 (3)
O5W—H9W···O3	0.88 (1)	1.94 (1)	2.810 (3)	169 (3)
O5W—H10W···O29W	0.88 (1)	1.91 (1)	2.772 (3)	169 (3)
O6W—H12W···O24W^{iv}	0.88 (1)	2.31 (1)	3.152 (4)	160 (3)
O7W—H13W···O18	0.87 (1)	2.18 (2)	2.936 (3)	146 (3)
O7W—H14W···O27^{iii}	0.87 (1)	2.10 (2)	2.919 (3)	157 (3)
O8W—H15W···O9^v	0.88 (1)	2.06 (2)	2.854 (3)	151 (3)
O8W—H16W···O7^v	0.87 (1)	2.23 (2)	2.992 (4)	146 (3)
O9W—H17W···O12	0.88 (1)	1.89 (1)	2.763 (3)	170 (3)

O9W—H18W···O31W	0.88 (1)	1.92 (1)	2.790 (3)	172 (3)
O10W—H20W···O25^{vi}	0.87	2.30	2.849 (4)	121
O10W—H20W···O27W^{vi}	0.87	2.38	3.203 (4)	158
O11W—H21W···O24^{vi}	0.88 (1)	2.59 (2)	3.355 (3)	147 (3)
O11W—H21W···O25^{vi}	0.88 (1)	2.15 (2)	2.964 (3)	154 (3)
O11W—H22W···O30W^{vii}	0.88 (1)	1.96 (1)	2.835 (3)	177 (3)
O12W—H23W···O16^{vii}	0.87 (1)	1.98 (1)	2.810 (3)	160 (3)
O12W—H24W···O14^{v}	0.87 (1)	1.89 (1)	2.747 (3)	170 (3)
O13W—H25W···O13	0.88 (1)	1.86 (1)	2.729 (3)	175 (4)
O13W—H26W···O16^{vii}	0.88 (1)	2.19 (2)	2.999 (3)	153 (3)
O14W—H27W···O9^{v}	0.88 (1)	2.05 (2)	2.877 (3)	156 (3)
O14W—H28W···O15^{vi}	0.87 (1)	1.90 (1)	2.777 (3)	176 (4)
O15W—H29W···O29W^{v}	0.88 (1)	1.89 (1)	2.758 (3)	170 (3)
O15W—H30W···O2^{v}	0.88 (1)	1.90 (1)	2.753 (3)	165 (3)
O16W—H31W···O3	0.88 (1)	2.01 (2)	2.829 (3)	155 (3)
O16W—H32W···O26^{iii}	0.87 (1)	1.93 (1)	2.797 (3)	174 (3)
O17W—H33W···O11	0.88 (1)	1.83 (1)	2.685 (3)	164 (4)
O17W—H34W···O3	0.87 (1)	2.06 (1)	2.900 (3)	160 (3)
O18W—H35W···O20	0.87 (1)	1.90 (1)	2.767 (3)	170 (3)
O18W—H36W···O32W^{v}	0.87 (1)	1.95 (1)	2.821 (3)	173 (3)
O19W—H37W···O6	0.88 (1)	2.22 (2)	2.946 (4)	140 (3)
O19W—H38W···O11	0.87 (1)	2.13 (2)	2.948 (3)	157 (3)
O20W—H39W···O1^{viii}	0.87 (1)	1.90 (1)	2.764 (3)	172 (4)
O20W—H40W···O6	0.87 (1)	2.11 (1)	2.937 (3)	159 (3)
O21W—H41W···O9W	0.88 (1)	2.26 (1)	3.112 (3)	165 (3)
O21W—H42W···O4^{v}	0.87 (1)	2.08 (1)	2.935 (3)	166 (3)
O22W—H43W···O28	0.87 (1)	2.10 (2)	2.899 (3)	152 (3)
O22W—H44W···O17^{iii}	0.88 (1)	2.17 (2)	2.955 (3)	148 (3)
O23W—H45W···O28	0.87 (1)	2.01 (1)	2.834 (3)	158 (3)
O23W—H46W···O22^{ix}	0.87 (1)	1.90 (1)	2.769 (3)	175 (4)
O24W—H47W···O24^{ii}	0.87 (1)	1.97 (2)	2.812 (3)	162 (3)
O24W—H48W···O30W^{iv}	0.88 (1)	1.91 (1)	2.787 (3)	177 (4)
O25W—H49W···O31W^{i}	0.87 (1)	2.04 (1)	2.907 (3)	170 (3)
O25W—H50W···O14^{i}	0.88 (1)	1.98 (1)	2.837 (3)	166 (3)
O26W—H51W···O23^{ii}	0.88 (1)	1.86 (1)	2.728 (3)	175 (3)
O26W—H52W···O5^{i}	0.88 (1)	2.23 (2)	3.017 (3)	149 (3)
O27W—H53W···O5^{i}	0.87 (1)	1.93 (1)	2.773 (3)	161 (3)
O27W—H54W···O25	0.88 (1)	1.89 (1)	2.759 (3)	171 (3)
O28W—H55W···O17^{iii}	0.88 (1)	1.86 (2)	2.720 (3)	166 (4)
O29W—H57W···O28^{iv}	0.88 (1)	1.92 (1)	2.783 (3)	169 (3)
O29W—H58W···O19^{ii}	0.87 (1)	1.97 (1)	2.839 (3)	171 (3)
O30W—H59W···O18	0.87 (1)	1.92 (2)	2.715 (3)	151 (3)
O30W—H60W···O13^{x}	0.88 (1)	2.42 (2)	3.206 (3)	149 (3)
O30W—H60W···O14^{x}	0.88 (1)	2.64 (2)	3.271 (3)	130 (3)
O31W—H61W···O6	0.87 (1)	1.91 (1)	2.735 (3)	158 (3)
O31W—H62W···O23^{vi}	0.88 (1)	2.52 (2)	3.300 (3)	149 (3)
O32W—H63W···O9	0.88 (1)	1.95 (1)	2.803 (3)	166 (3)
O32W—H64W···O4	0.88 (1)	2.08 (1)	2.948 (3)	172 (3)
N2—H80···O1	0.94 (4)	1.68 (4)	2.496 (4)	144 (3)
N4—H81···O8	0.87 (4)	1.75 (4)	2.506 (3)	143 (4)

N6—H82⋯O15	0.92 (4)	1.66 (4)	2.493 (3)	149 (4)
N8—H83⋯O22	0.90 (4)	1.72 (4)	2.489 (4)	141 (4)

Symmetry codes: (i) −x+1, −y, −z+1; (ii) x−1, y, z; (iii) −x+1, −y+1, −z+1; (iv) −x, −y+1, −z+1; (v) x+1, y, z; (vi) −x+2, −y, −z+1; (vii) x+1, y−1, z; (viii) −x+1, −y, −z+2; (ix) −x+1, −y+1, −z; (x) x−1, y+1, z.

Table 10
Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1W⋯O4^i	0.88 (1)	1.95 (1)	2.814 (3)	171 (3)
O1W—H2W⋯O6	0.87 (1)	1.99 (1)	2.837 (3)	165 (3)
O2W—H3W⋯O6	0.87 (1)	2.08 (2)	2.863 (3)	150 (2)
O2W—H4W⋯O2^{ii}	0.87 (1)	2.01 (2)	2.807 (3)	152 (3)
O3W—H5W⋯O7	0.88 (1)	2.00 (1)	2.864 (3)	170 (3)
O3W—H6W⋯O3^{iii}	0.88 (1)	1.96 (1)	2.816 (3)	164 (3)
O4W—H7W⋯O9W	0.87 (1)	2.14 (3)	2.913 (7)	148 (4)
O4W—H8W⋯O2^{ii}	0.87 (1)	1.99 (2)	2.832 (3)	164 (4)
O5W—H9W⋯O2^{iii}	0.88 (1)	2.10 (1)	2.966 (2)	169 (3)
O5W—H10W⋯O5^{iv}	0.87 (1)	2.13 (2)	2.949 (3)	156 (3)
O6W—H11W⋯O9W	0.87 (1)	2.13 (1)	2.983 (5)	168 (3)
O6W—H11W⋯O10W	0.87 (1)	2.09 (2)	2.923 (10)	161 (4)
O6W—H12W⋯O5^{ii}	0.88 (1)	1.96 (1)	2.839 (3)	175 (4)
O7W—H13W⋯O6W^v	0.86 (1)	2.36 (2)	3.042 (3)	136 (3)
O7W—H13W⋯O9W^v	0.86 (1)	2.47 (2)	3.211 (6)	144 (3)
O7W—H14W⋯O3^i	0.87 (1)	1.90 (1)	2.753 (3)	169 (4)
O8W—H15W⋯O5^{ii}	0.87 (1)	2.41 (2)	3.199 (3)	151 (3)
O8W—H16W⋯O1^{vi}	0.87 (1)	1.92 (1)	2.790 (3)	178 (3)
O9W—H17W⋯O7^{vii}	0.89 (1)	1.97 (2)	2.830 (5)	164 (4)
O9W—H18W⋯O7^{ii}	0.89 (1)	2.10 (2)	2.904 (6)	150 (4)
O9W—H18W⋯O9W^{viii}	0.89 (1)	2.19 (4)	2.820 (11)	127 (4)
N2—H1N⋯O1	0.88 (3)	1.74 (3)	2.495 (3)	142 (3)

Symmetry codes: (i) x−1, y−1, z; (ii) x−1, y, z; (iii) −x+2, −y+2, −z+1; (iv) −x+1, −y+1, −z+1; (v) −x, −y+1, −z+1; (vi) −x+2, −y+2, −z+2; (vii) −x+1, −y+2, −z+1; (viii) −x, −y+2, −z+1.

Table 11
Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1W⋯O7^i	0.86 (1)	2.05 (1)	2.906 (2)	174 (3)
O1W—H2W⋯O2^{ii}	0.86 (1)	2.33 (2)	3.075 (2)	146 (2)
O1W—H2W⋯O3^{ii}	0.86 (1)	2.33 (2)	3.107 (2)	151 (2)
O2W—H3W⋯O1S	0.86 (1)	2.02 (1)	2.854 (2)	162 (2)
O2W—H4W⋯O5^{iii}	0.86 (1)	2.11 (1)	2.891 (2)	150 (2)
O3W—H5W⋯O4^{iv}	0.87 (1)	1.97 (1)	2.791 (2)	158 (2)
O3W—H6W⋯O2^{ii}	0.87 (1)	1.96 (1)	2.789 (2)	160 (2)
N2—H1N⋯O1	0.86 (3)	1.75 (3)	2.490 (2)	143 (3)

Symmetry codes: (i) −x+1, y+1/2, −z+1/2; (ii) −x+1, y−1/2, −z+1/2; (iii) −x+2, y+1/2, −z+1/2; (iv) −x+2, y−1/2, −z+1/2.

Table 12

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O1	0.88 (1)	2.17 (3)	3.011 (19)	161 (6)
O2*W*—H1*W*···O1	0.88 (1)	2.17 (3)	2.85 (3)	134 (6)
O1*W*—H2*W*···O7[i]	0.88 (1)	2.07 (1)	2.903 (17)	158 (6)
O2*W*—H2*W*···O7[i]	0.88 (1)	2.07 (1)	2.93 (2)	169 (7)
N2—H1*N*···O1	0.90 (1)	1.66 (3)	2.477 (4)	148 (5)

Symmetry code: (i) *x*−1, *y*, *z*.

Table 13

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O7[i]	0.87 (1)	1.86 (2)	2.718 (5)	166 (5)
O1*W*—H2*W*···O4	0.87 (1)	2.06 (4)	2.769 (5)	138 (5)
N2—H1*N*···O1	0.84 (6)	1.75 (5)	2.479 (6)	143 (5)

Symmetry code: (i) −*x*+1/2, *y*−1/2, −*z*+3/2.

Table 14

Selected bond lengths (Å) for PX anions. Literature data for typical hydroxy tautomer and azo species are given for comparison and are taken from (Kennedy *et al.*, 2001).

Structure	I	II	III	III	IV	V	VI	VII	hydroxy-azo	azo
Metal atom	Mg	Ca	Sr	Sr	Co	Ni	Cu	Zn	Na	Na
N-N	1.304 (3)	1.293 (3)	1.304 (6)	1.293 (6)	1.307 (3)	1.302 (11)	1.294 (7)	1.302 (9)	1.281 (4)	1.253 (2)
C-N	1.335 (4)	1.344 (3)	1.343 (6)	1.352 (6)	1.339 (3)	1.336 (13)	1.332 (8)	1.341 (9)	1.392 (4)	1.418 (2)
C-N(H)	1.414 (4)	1.408 (3)	1.403 (6)	1.419 (6)	1.409 (3)	1.396 (13)	1.412 (8)	1.406 (9)	1.414 (5)	1.430 (2)
C-C(O)	1.464 (4)	1.445 (3)	1.445 (7)	1.449 (7)	1.457 (3)	1.478 (15)	1.459 (9)	1.453 (11)	1.413 (5)	1.398 (3)
C-O	1.261 (3)	1.265 (3)	1.276 (6)	1.274 (6)	1.263 (3)	1.271 (11)	1.273 (7)	1.264 (9)	1.343 (4)	n.a.

Table 15

Selected bond lengths (Å) for CS anions. Literature data for typical hydroxy tautomer and azo species are given for comparison and are taken from (Kennedy *et al.*, 2001).

Structure	VIII	VIII	VIII	VIII	IX	*X*	XI	XII	hydroxy-azo	azo
Metal atom	Ca	Ca	Ca	Ca	Sr	Ba	Cu	Zn	Na	Na
N-N	1.298 (4)	1.297 (4)	1.301 (4)	1.296 (4)	1.292 (3)	1.298 (2)	1.303 (5)	1.301 (6)	1.281 (4)	1.253 (2)
C-N	1.346 (4)	1.341 (4)	1.344 (4)	1.342 (4)	1.338 (3)	1.340 (3)	1.327 (5)	1.338 (7)	1.392 (4)	1.418 (2)
C-N(H)	1.412 (4)	1.403 (4)	1.406 (4)	1.408 (4)	1.403 (3)	1.402 (3)	1.393 (5)	1.406 (7)	1.414 (5)	1.430 (2)
C-C(O)	1.457 (4)	1.460 (4)	1.462 (4)	1.463 (4)	1.451 (3)	1.464 (3)	1.460 (5)	1.473 (7)	1.413 (5)	1.398 (3)
C-O	1.269 (4)	1.268 (4)	1.275 (4)	1.267 (4)	1.266 (3)	1.259 (3)	1.281 (5)	1.260 (7)	1.343 (4)	n.a.

References

Agilent (2014). *CrysAlis PRO*. Agilent Technologies Ltd., Yarnton, Oxfordshire, England.

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Beko, S. L., Hammer, S. M. & Schmidt, M. U. (2012). *Angew. Chem. Int. Ed.* **51**, 4735-4738.

Chen, H.-X., Zhou, F., Ma, Y., Xu, X.-P., Ge, J.-F., Zhang, Y., Xu, Q.-F. & Lu, J.-M. (2013). *Dalton Trans.* **42**, 4831-4839.

Christie, R. M. & MacKay, J. L. (2008). *Color. Technol.* **124**, 133-144.

Cole, S. J. & Gale, P. A. (2012). *Chem. Sci.* **3**, 683–689.

Cote, A. P. & Shimizu, G. K. H. (2003). *Coord. Chem. Rev.* **245**, 49–64.

Dodds, C. A., Hobday, C., Kennedy, A. R., McKellar, S. C., Smillie, K. & Walls, A. (2017). *New J. Chem.* **41**, 1574–1581.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Gorelik, T., Schmidt, M. U., Bruning, J., Beko, S. & Kolb, U. (2009). *Cryst. Growth Des.* **9**, 3898–3903.

Grzesiak-Nowak, M., Oszajca, M., Rafalska-Lasocha, A., Goszczycki, P., Ostrowska, K. & Lasocha, W. (2019). *Dyes Pig.* **160**, 252-258.

Hao, Z. & Iqbal, A. (1997). Chem. Soc. Rev., 26, 203–213.

Ivashevskaya, S. N., van de Streek, J., Djanhan, J. E., Bruning, J., Alig, E., Bolte, M., Schmidt, M. U., Blaschka, P., Hoffken, H. W. & Erk, P. (2009). *Acta Cryst.* B**65**, 212–222.

Kennedy, A. R., Andrikopoulos, P. C., Arlin, J.-B., Armstrong, D. R., Duxbury, N., Graham, D. V. & Kirkhouse, J. B. A. (2009). *Chem. Eur. J.* **15**, 9494–9504.

Kennedy, A. R., Hughes, M. P., Monaghan, M. L., Staunton, E., Teat, S. J. & Smith, E. W. (2001). *J. Chem. Soc. Dalton Trans.*, 2199-2205.

Kennedy, A. R., Kirkhouse, J. B. A., McCarney, K. M., Puissegur, O., Smith, W. E., Staunton, E., Teat, S. J., Cherryman, J. C. & James, R. (2004). *Chem. Eur. J.* **10**, 4606–4615.

Kennedy, A. R., Kirkhouse, J. B. A. & Whyte, L. (2006). *Inorg. Chem.* **45**, 2965-2971.

Kennedy, A. R., McKellar, S. C. & Okoth, M. O. (2010). *Acta Cryst.* E**66**, m1330-m1331.

Kennedy, A. R., McNair, C., Smith, W. E., Chisholm, G. & Teat, S. J. (2000). *Angew. Chem. Int. Ed.* **39**, 638-640.

Kennedy, A. R., Stewart, H., Eremin, K. & Stenger, J. (2012). *Chem. Eur. J.* **18**, 3064–3069.

Lu, J., Gao, S.-Y., Lin, J.-X., Shi, L.-X., Cao, R. & Batten, S. R. (2009). *Dalton Trans.* 1944-1953.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Mahmudov, K. T., Sutradhar, M., Martins, L. M. D. R. S., Guedes da Silva, F. C., Ribera, A., Nunes, A. V. M., Gahramanova, S. I., Marchetti, F. & Pombeiro, A. J. L. (2015). *RSC Adv.* **5**, 25979–25987.

Oh, I.-H., Park, G. & Park, S.-H. (2017). *Z. Kristallogr. New Cryst. Struct.* **232**, 803–805.

Ojala, W. H., Gleason, W. B., Richardson, T. I. & Lovrien, R. E. (1994*a*). *Acta Cryst.* C**50**, 1615-1620.

Ojala, W. H., Lu, L. K., Albers, K. E., Gleason, W. B., Richardson, T. I., Lovrien, R. E. & Sudbeck, E. A. (1994*b*). *Acta Cryst.* B**50**, 684-694.

Rigaku (2015). *CrystalClear*. Rigaku MSC, Orem, Utah USA.

Schmidt, M. U., van de Streek, J. & Ivashevskaya, S. N. (2009). *Chem. Eur. J.* **15**, 338–341.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Stahl, P. H. & Wermuth, C. G. (2008). Eds. *Handbook of Pharmaceutical Salts: Properties, Selection and Use*. VHCA: Zurich.

Zollinger, H. (2003). *Color Chemistry: Synthesis, Properties, and Applications of Organic Dyes and Pigments. 3rd Edition*. Wiley-VCH: Zurich.

Figure 1

Molecular structure of (I), $[Mg(OH_2)_6][PX] \cdot DMF$, with non-H atoms shown as 50% probability ellipsoids. H atoms are drawn as small spheres of arbitrary size. For clarity, the disordered DMF solvent and disordered methyl H atoms are not shown.

Figure 2

Molecular structure of (II), $[Ca(OH_2)_7][PX] \cdot 2.5H_2O$, with non-H atoms shown as 50% probability ellipsoids. For clarity, most H atoms and the minor disorder components are not shown.

Figure 3

Part of the structure of (III), $[Sr(PX)(DMF)_2(OH_2)_{0.5}]_n$, with non-H atoms shown as 50% probability ellipsoids. For clarity, most H atoms and the minor disorder components of the solvent ligands are not shown. Full atom numbering scheme is available from the supplementary cif file.

Figure 4

View showing part of the one-dimensional coordination polymer of (III), $[Sr(PX)(DMF)_2(OH_2)_{0.5}]_n$.

Figure 5

Molecular structure of (IV), $[Co(OH_2)_6][PX] \cdot DMF$, with non-H atoms shown as 50% probability ellipsoids. H atoms are drawn as small spheres of arbitrary size. For clarity, the disordered DMF solvent and disordered methyl H atoms are not shown. Structures (V) to (VII) are the isostructural Ni, Cu and Zn compounds. Figures showing their displacement ellipsoids are available as supplementary information.

Figure 6

Molecular structure of one of the four crystallographically unique cation-anion pairs in structure (VIII), $[Ca(OH_2)_7]$ $[CS] \cdot H_2O$, with non-H atoms shown as 50% probability ellipsoids. H atoms are drawn as small spheres of arbitrary size. Full atom numbering scheme is available from the supplementary cif file.

Figure 7

Molecular structure of (IX), $[Sr(OH_2)_8][CS] \cdot H_2O$, with non-H atoms shown as 50% probability ellipsoids. H atoms are drawn as small spheres of arbitrary size. For clarity, the disordered position of the water of crystallization is not shown.

Figure 8

Asymmetric unit contents of (*X*), $[Ba(CS)(DMF)(OH_2)_3]_n$, with non-H atoms shown as 50% probability ellipsoids. H atoms are drawn as small spheres of arbitrary size.

Figure 9

Part of the one-dimensional coordination polymer structure of (*X*), $[Ba(CS)(DMF)(OH_2)_3]_n$.

Figure 10

Molecular structure of (XI), $[Cu((CS)(DMF)_4]\cdot H_2O$, with non-H atoms shown as 50% probability ellipsoids. For clarity, most H atoms and the solvent water molecule are not shown.

Figure 11

Unique part of the polymeric structure of (XII), $[Zn(CS)(DMF)_3(OH_2)]_n.n/2\ Et_2O$, with non-H atoms shown as 50% probability ellipsoids. For clarity, most H atoms and the solvent ether molecule are not shown.

Figure 12

Part of the one-dimensional coordination polymer structure of (XII), $[Zn(CS)(DMF)_3(OH_2)]_n.n/2\ Et_2O$.

Figure 13

Packing view of (I), $[Mg(OH_2)_6][PX]\cdot DMF$, viewed down the b direction. Note the alternate layers of azo anion and layers containing cations with solvent.

Figure 14

Packing view of (IX), $[Sr(OH_2)_8][CS]\cdot H_2O$, viewed down the a direction.

Figure 15

Packing view of (XII), $[Zn(CS)(DMF)_3(OH_2)]_n.n/2\ Et_2O$, viewed down the b direction.