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Interaction of Colorformers and Coreactants. Part I. First Crystal Structures of the Colorforming Species Composed of Crystal Violet Lactone and Metal Iodides

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ABSTRACT

The first crystalline adducts of a colorformer and coreactants have been synthesized. Crystal Violet Lactone (CVL) reacted with zinc and cadmium iodide, respectively, in acetone solution to form well defined complexes. ^{13}C *NMR, X-ray and crystallographic data have been collected on these complexes. They indicated an ionic structure of* $[2\ CVL \cdot 3ZnI_2 \cdot acetone]$ *with a* Zn_2I_3*-moiety rigidly held in place by two encompassing symmetrically situated carboxylate units. A polymeric structure was found for* $[CVL \cdot 3CdI_2 \cdot 1/2\ acetone]$*. The CVL part with its open carboxylate structure is embedded in a carrier matrix built of cadmium and of iodine atoms, forming alternately six- and four-membered rings which are linked with each other in a spiro- arrangement. Intercalated acetone molecules were found to be a prerequisite for the formation of single crystals.*

1 INTRODUCTION

In the early 1950s the National Cash Register Corporation introduced the revolutionary process of carbonless copying paper.[1] Although the practical

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Deposition data available on request from publisher.

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application and the adherent technical manipulations have since undergone considerable changes, the original idea of the colorforming step has not progressed much beyond the recognition of a triphenylmethyl carbonium ion being involved. Yet the technical innovations in the carbonless copying paper business have multiplied[2] over the past 30 years, primarily documented in the ever expanding and competitive patent literature, and intermittent displays of marketing surveys,[3,4] but very little attention has been devoted to the detailed structural requirements of a successful interface of colorformers and coreactants.

An investigation of a reversible cleavage of the lactone ring upon adsorption of the phthalide dyestuffs on the surface of alkali or alkaline earth salts was pioneered by Kortuem & Vogel in 1960.[5] They showed convincingly that cleavage of the lactone ring may be caused by the polarizing effect of the cations on the surface of the metal halide crystal lattice.

No significant contribution as to the structural details of the adsorbed species has been put forward in the ensuing years.

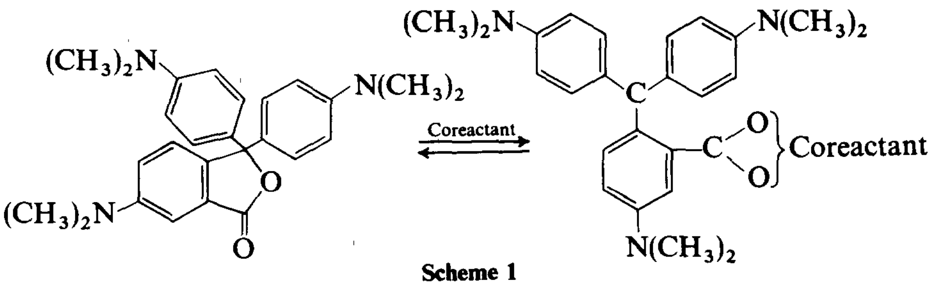
The acid induced cleavage of a colorless moiety was also effected with protonic acids such as phenols, salicylic acids or with acidic clays.[1] Considerable improvements[6] were made by using water soluble metals salts, such as zinc halides intermixed with oil soluble resin particles. The application of other metallic ions such as aluminum, cadmium, calcium and strontium was likewise supposed to improve fade resistance and give similar print intensity.[7] Yet more efficient developments in technical applications have been realized when zinc salicylates, notably 3,5-disubstituted derivatives thereof, were first incorporated into these systems.[7]

The idea of a metal cluster which may have been formed from Crystal Violet Lactone and bis(3,5-di-tert.-butylsalicylate)zinc salt was advanced and postulated, stemming from the results of investigating the stoichiometry of this reaction in toluene as solvent using Job's method.[8] The results obtained favoured the idea and has borne out the conception of an organometallic cluster of the type $[\mathrm{Zn_3(salicylate)_5(CVL)}]^{\oplus}$ $\mathrm{salicylate}^{\ominus}$ which was proposed to explain the formation and the existence of a colored species in solution.

We now present two examples, the X-ray structural elucidation of which can considerably ease the discussion of the much presumed, yet never proven, composition of colorformers and their host matrices, both of which are responsible for an efficient rendering of color formation.

The principles of this new insight into the molecular details of the solid state structure of the colorforming molecules with their attached coreactants are explained and illustrated with these examples.

We have selected two compounds, both of which are composed of Crystal



Scheme 1

Violet Lactone (CVL) (**1**), but with different coreactants, and each displaying a singularly representative structure of those combinations.

Crystal Violet Lactone undergoes instantaneous reaction with zinc or cadmium halides, yielding well defined, crystalline colored complexes displaying an 'open lactone' structure, e.g. a carboxylate moiety, such as shown in Scheme 1.

2 RESULTS AND DISCUSSION

The selection of Crystal Violet Lactone and its zinc or cadmium complexes for a determination of their molecular structure by X-ray analysis was suggested by a number of factors such as their perfect and excellent crystallinity and a favorable tendency to form single crystals which are not interspersed with large irregular aggregates. The latter factor was most cumbersome to overcome in the preparation of the complexes. Further difficulties in obtaining single crystals arose from the necessity of having to manipulate rather concentrated solutions because of the tendency of these complexes to dissociate in solution.

The reaction of Crystal Violet Lactone with zinc halides using acetone as the solvent led to the formation of the respective iodonium, brominium and chloronium salts **2a–c**, **a** = I, **b** = Br, **c** = Cl.

$$\mathbf{2a} = 2\,\mathrm{CVL}\cdot 3\,\mathrm{ZnI_2}\cdot\mathrm{acetone}$$
$$\mathbf{2b} = 2\,\mathrm{CVL}\cdot 3\,\mathrm{ZnBr_2}\cdot\mathrm{acetone}$$
$$\mathbf{2c} = 2\,\mathrm{CVL}\cdot 3\,\mathrm{ZnCl_2}\cdot\mathrm{acetone}$$

Compounds **2a–c** are stable in the crystalline state. Although **2a–c** were prepared in acetone using high concentrations of the reactants, they revert quantitatively to Crystal Violet Lactone on diluting these solutions. Generally, attempts to recrystallize **2a–c** from solvents led to extensive decomposition; only **2a** could be recrystallized from very concentrated solutions in acetone, with considerable loss of product. The structure of **2a** is shown in Fig. 1. The iodonium compound (**2a**) appeared in solution to be the

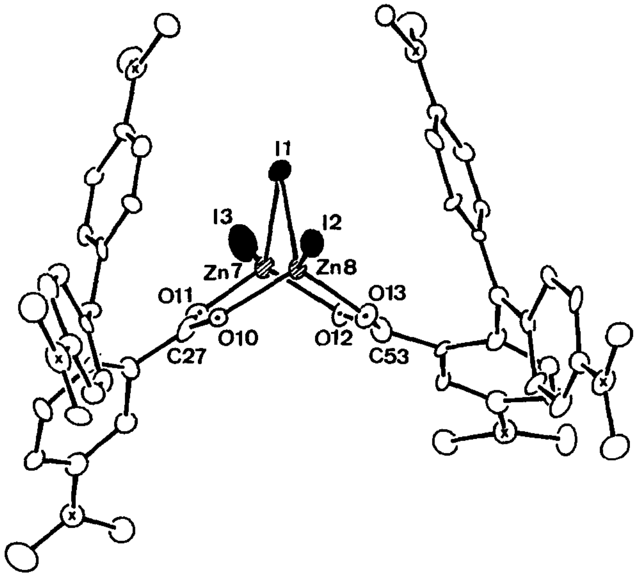


Fig. 1. Perspective drawing of the molecular structure of the cationic part of **2a** (● Iodine, ▨ Zinc, ⊙ Oxygen, ⊗ Nitrogen).

most stable one, as judged from the ^{13}C NMR spectra. It displayed distinct signals in concentrated solutions of deuteromethylene chloride, whereas **2b** or **2c** showed broad signals which rendered them useless for interpretation.

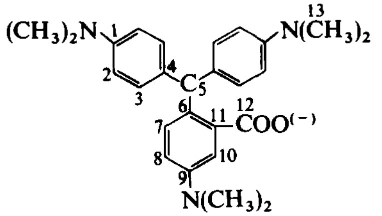
The Crystal Violet Lactone–cadmium iodide complex (**3**) [$2 \cdot CVL \cdot 6CdI_2 \cdot$ acetone] showed a more pronounced tendency to form single crystals than the zinc iodide counterpart. Again, extensive disintegration in dilute solution was noticed, paralleling the instability of **2a**. The structure of **3** is shown in Fig. 5.

All attempts to obtain single crystals from Crystal Violet Lactone and zinc salicylate were unsuccessful. Only non-crystalline aggregates were formed, regardless of the solvent in which the reaction was performed. By using metallic iodides however, we can demonstrate the molecular state in which the color rendering part of the molecule exists.

2.1 IR and ^{13}C NMR results

The absence of the prominent absorption band in the infrared spectra of **2a–c** and of **3** at 1755 cm^{-1}, which is known to be due to the lactone frequency, and its replacement by a rather strong and broad absorption band at 1579 cm^{-1}, indicated a carboxylate structure. This band, however, was partially superimposed by the absorption of the phenyl rings. The strong band at 1172 cm^{-1} could be assigned to the N-phenyl stretching

TABLE 1
^{13}C NMR Data for **2a**



^{13}C NMR 156·71 C(1), 113·59 C(2), 140·49 C(3), 128·52 C(4), 179·32 C(5), 127·30 C(6), 138·61 C(7), 112·40 C(8), 153·80 C(9), 115·01 C(10), 143·87 C(11), 175·06 C(12), 41·05, 40·81 C(13)

vibration. The main vibrational absorption frequencies and the assignments could be correlated, and proved to be identical with those reported for the Crystal Violet cation.[9] A very small absorption at 1698 cm^{-1} indicates the carbonyl frequency of the acetone molecule.

The iodine complex **2a** proved to be rather stable in solution in deuteromethylene chloride, which was selected as a solvent for obtaining the ^{13}C NMR spectra. The results are detailed in Table 1. They show, for the central carbon atom C-5, the expected value of $\delta = 179{\cdot}3$ ppm for the sp^2-species, which correlated well with the reported value for the Crystal Violet cation which has the corresponding signal at $\delta = 176{\cdot}9$ ppm.[10] The two signals at 41·05 and at 40·81 ppm (at 25°C), indicated the non-equivalency of the two methyl groups attached to the nitrogen atoms, thus giving supporting evidence for a partial quinone structure of the dimethylamino moiety. However, inspection of the bond lengths 1·42–1·45 Å,[11] of the crystalline species gave no definite indication of a quinone-like structure in the solid state. The ^{13}C NMR spectrum of 3 was identical with that of **2a**.

2.2 Solid state structure of 2a

The results of the X-ray diffraction studies are illustrated in Figs 1–4. The molecular structure of **2a** is shown in Figs 1, 2 and 3, and the packing diagram is illustrated in Fig. 4.

The cationic molecular part (Fig. 1) contains two triphenylmethyl carbonium ion groups which are linked via their carboxylate units to the central part which is composed of a Zn_2I_3-moiety. This part has a non-crystallographic plane of symmetry encompassing the atoms I(1), I(2), I(3), Zn(7) and Zn(8). The zinc atoms are four coordinate and have a nearly tetrahedral geometry, each being bonded to the two iodine and two oxygen

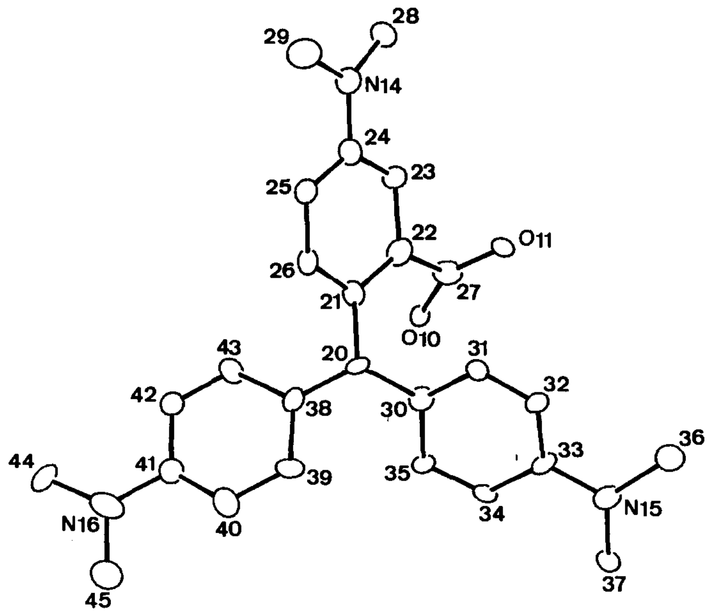


Fig. 2. Triphenylmethyl carbonium ion in the right-handed propeller form. (Deviations from the sp^2-Plane: C(22) −0·75 Å; C(26) 0·87 Å; C(31) −0·48 Å; C(35) −0·62 Å; C(43) −0·53 Å.)

atoms, with I-Zn-I angles of 114·2–117·5°. Selected bond angles are compiled in Table 2.

The Zn_2I_3-moiety is planar within 0·09 Å, and rigidly held in place by two encompassing carboxylate units forming angles of 57° with C(27), O(10), O(11), and of −69° with C(53), O(12) and O(13), respectively. The

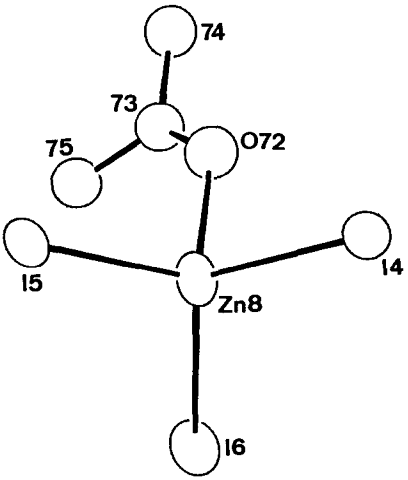


Fig. 3. Molecular structure of the anion [ZnI_3 Acetone].

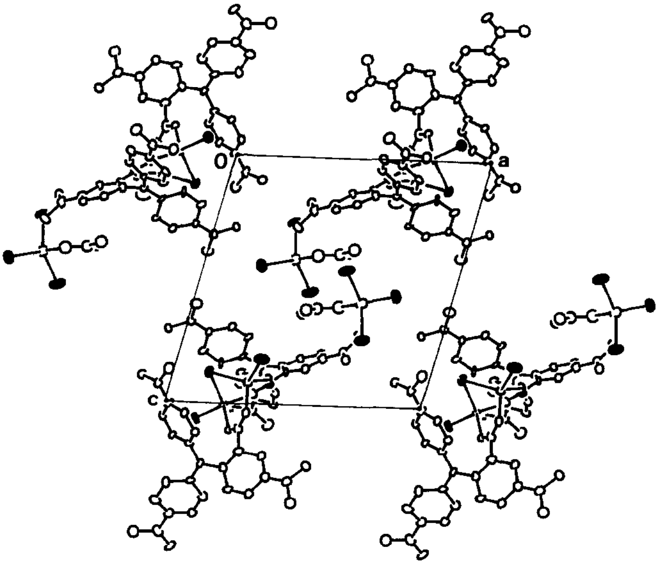


Fig. 4. Packing diagram of **2a** (for clarity iodine atoms are shaded).

TABLE 2
Selected Bond Angles of **2a**

Atom 1	*Atom 2*	*Atom 3*	*Angle* (°)
Zn7	I1	Zn8	75·5 (2)
I1	Zn7	I3	116·4 (2)
I1	Zn7	O11	106·4 (9)
I1	Zn7	O12	103·9 (8)
I3	Zn7	O11	110 (1)
I3	Zn7	O12	111 (1)
O11	Zn7	O12	108 (1)
I1	Zn8	I2	114·9 (3)
I1	Zn8	O10	103·5 (9)
I1	Zn8	O13	105 (1)
I2	Zn8	O10	108·1 (9)
I2'	Zn8	O13	116·1 (1)
O10	Zn8	O13	108 (1)
I4	Zn9	I5	114·2 (3)
I4	Zn9	I6	117·5 (4)
I4	Zn9	O72	95 (1)
I5	Zn9	I6	115·0 (4)
I5	Zn9	O72	106 (1)
I6	Zn9	O72	106 (1)

TABLE 3

Selected Bond Lengths of **2a**

Atom 1	*Atom 2*	*Distance*	*Atom 1*	*Atom 2*	*Distance*
I1	Zn7	2·615 (6)	O11	C27	1·21 (7)
I1	Zn8	2·661 (6)	O12	C53	1·29 (6)
I2	Zn8	2·509 (7)	O13	C53	1·23 (7)
I3	Zn7	2·523 (8)	N14	C24	1·42 (7)
I4	Zn9	2·55 (1)	N14	C28	1·49 (7)
I5	Zn9	2·528 (8)	N14	C29	1·42 (6)
I6	Zn9	2·56 (1)	N15	C33	1·44 (6)
Zn7	O11	1·91 (3)	N15	C36	1·50 (8)
Zn7	O12	1·95 (3)	N15	C37	1·43 (6)
Zn8	O10	2·00 (2)	N16	C41	1·45 (8)
Zn8	O13	1·99 (3)	N16	C44	1·48 (7)
Zn9	O72	2·13 (6)	N16	C45	1·47 (8)
O10	C27	1·27 (6)			

zinc–iodine distances to the bridged iodine atoms are 2·615 Å and 2·661 Å, respectively, and thus significantly larger than the two zinc–iodine terminal bonds which have bond lengths of 2·509–2·503 Å. The Zn(7)–Zn(8) distance is 3·23 Å, which is considerably larger than the Zn–Zn bond length of 2·665 Å in zinc metal. Further selected bond lengths are displayed in Table 3.

These data correlate well with the known data of Zn–I bond distances (2·56–2·68 Å) quoted in the literature.[12,13]

Figure 2 shows one of the triphenylmethyl molecular units with the carboxylate group attached. The atoms C(20), C(21), C(30) and C(38) are each situated in an sp^2-plane, and the same holds true for the opposite triphenylmethyl moiety. Dihedral angles between the phenyl rings and, their attached carboxylate groups, are compiled in Table 4.

Each molecule consists of one left and one right handed propeller. The propeller blades of **2a** are neither arranged in any symmetrical order of twist

TABLE 4

Selected Angles of the Phenyl Rings with the sp^2-Plane of **2a**

C20, C21, C30, C38	Phenyl C21	C26	43°	54°
C20, C21, C30, C38	Phenyl C30	C35	27°	31°
C20, C21, C30, C38	Phenyl C38	C43	28°	18°
Phenyl C21 ... C26	Carboxyl C22, C27, O10, O11		45°	25°

For the numbering of the carbon atoms refer to Fig. 2. Data for the second part of the cation.

around the central carbon atom, nor do they exhibit any indication of a mirror image with respect to each other.

X-ray analysis of the related crystalline triphenylmethyl carbonium perchlorate exhibited three phenyl groups in symmetrical propeller conformation with an angle of twist of 31·8 ± 0·6° for each of the propeller blades showing a D_3-symmetry.[14] A coplanar geometry required for maximum resonance stabilization is prevented by steric interference between ortho-hydrogen atoms in neighboring rings. Models have been suggested for maximum resonance stabilization and requirements for minimum steric repulsion.[15]

Furthermore, a report on the X-ray structure of tris-*p*-aminotriphenylmethylcarbonium perchlorate indicated that although the ion is propeller shaped, one of the phenyl rings is twisted out of the plane by 28°, the others having an angle each of 34°.[15,16]

The arrangement of the substituents around the nitrogen atoms of **2a** is either a planar one or tends to be slightly pyramidal. Atomic distances of the nitrogen atoms from the plane formed by the adjacent carbon atoms range from 0·01 Å to 0·11 Å. The angle between the dimethylamino groups and the phenyl rings are between 0 and 13°. Comparable values were also found to prevail in structurally related molecular moieties.[17]

The N–C bond length varies between 1·39 and 1·45 Å, as compared to 1·47 Å which is the sum of the respective covalent radii, thus implying only negligibly small contributions from resonance forms involving the dimethylamino group. Also the distances from the central carbon atoms C(20) and C(20)′, respectively, to their respective phenyl rings have very little double bond character, since their average length was found to be 1·42 Å as compared to a $C(sp^2)$–$C(sp^2)$ bond length of 1·48 Å.[18,19]

The Zn_2I_3-moiety introduces a positive charge onto the entire system, with the anion $[ZnI_3\text{acetone}]^{\ominus}$ being the negative counterpart. This anion is represented in Fig. 3. There is a tetrahedral environment about the zinc atom with Zn–I distances of 2·528–2·56 Å. The Zn–O distance was found to be 2·13 Å, and thus larger than the other Zn–O bond distances with 1·91–2·00 Å. Good correlation was found with the known Zn–O distance of 2·12 Å which was reported for the $[ZnCl_3(CH_3)_2CO]^{\ominus}$ anion.[20]

Thus, adsorption and/or occlusion of a suitable solvent molecule during growth of crystals from solutions is dictated by the symmetry and the structure of the crystal lattices, which either occluded the solvent molecules (see **3** as an example), or held it bound as a coordinate partner, as shown in Fig. 3 representing the zinc triiodide acetone moiety.

The molecular packing is shown in Fig. 4, indicating individual ions with no short range interactions with each other.

2.3 Solid state structure of [CVL·3CdI$_2$·Acetone] (3)

We have selected a further example of Crystal Violet Lactone with cadmium iodide as the coreactant. We deemed this example of particular interest, because the combination of both compounds revealed a molecular structure which was entirely different from that found for **2a**.

The lactone ring of Crystal Violet Lactone and of other colorformers also, undergoes equally facile ring opening of the lactone ring by using cadmium iodide.

Acetone solvate single crystals were obtained from a solution of Crystal Violet Lactone and cadmium iodide in acetone. Several perspective drawings of the solvate, along with the atom-labelling scheme are shown in Figs 5, 6 and 7.

Figure 5 reveals the polymeric features of the backbone of the carrier matrix cadmium iodide. Cadmium and iodine atoms are alternately bound to each other, forming six-membered rings which are linked in a spiro arrangement by interspaced four membered rings which are on centers of symmetry. One of the six iodine atoms is singly bonded and the others are twofold coordinated to the cadmium atoms. Two cadmium atoms each are bonded to four iodine atoms, and each third cadmium atom is surrounded by three iodine atoms, and in addition bound to one of the oxygen atoms of the carboxylate group, which thus serves as the fourth substituent of the tetrahedral environment of Cd(9). Figure 6 shows the atom numbering and

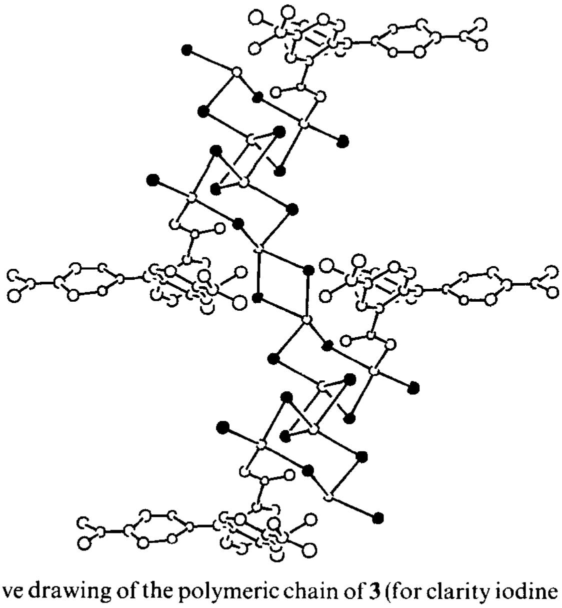


Fig. 5. Perspective drawing of the polymeric chain of **3** (for clarity iodine atoms are shaded).

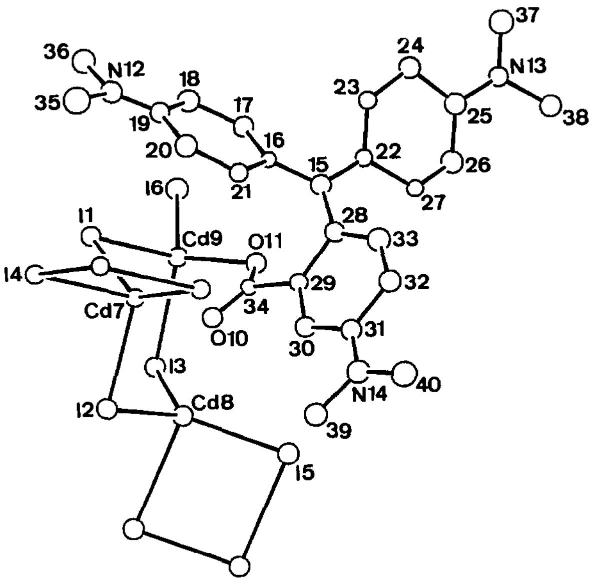


Fig. 6. Perspective drawing of the atom numbering of **3**. (Deviations from the sp^2-plane C(17) −0·59 Å; C(21) 0·70 Å C(23) 0·58 Å; C(27) 0·36 Å; C(29) −0·88 Å; C(33) 0·94 Å.)

the structural attachment of the carboxylate group onto the cadmium atom. Tables 5 and 6 contain the respective selected bond lengths and bond angles for the heavy atoms.

The cadmium–iodine distances in the six membered ring were found to be between 2·775 and 2·838 Å, thus indicating a slightly distorted chair form.

TABLE 5
Selected Bond Lengths of **3**

Atom 1	*Atom 2*	*Distance*	*Atom 1*	*Atom 2*	*Distance*
I1	CD7	2·835 (4)	CD8	O10	2·69 (3)
I1	CD9	2·828 (4)	O10	C34	1·17 (5)
I2	CD7	2·822 (5)	O11	C34	1·26 (4)
I2	CD8	2·775 (4)	N12	C19	1·32 (6)
I3	CD8	2·781 (4)	N12	C35	1·50 (6)
I3	CD9	2·838 (5)	N12	C36	1·48 (7)
I4	CD7	2·974 (4)	N13	C25	1·39 (5)
I4′	CD7	2·796 (4)	N13	C37	1·37 (7)
I5	CD8	2·727 (5)	N13	C38	1·54 (6)
I5′	CD8	3·079 (6)	N14	C31	1·28 (5)
I6	CD9	2·696 (4)	N14	C39	1·49 (7)
CD7	O10	2·41 (2)	N14	C40	1·48 (7)
CD9	O11	2·20 (3)			

TABLE 6
Selected Bond Angles of **3**

Atom 1	*Atom 2*	*Atom 3*	*Angle* (°)
CD7	I1	CD9	96·0 (1)
CD7	I2	CD8	89·2 (2)
CD8	I3	CD9	95·0 (1)
CD7	I4	CD7′	89·9 (1)
CD8	I5	CD8′	85·0 (2)
I1	CD7	I2	109·2 (2)
I1	CD7	I4	90·1 (1)
I1	CD7	I4′	143·2 (2)
I1	CD7	O10	86·6 (5)
I2	CD7	I4	93·1 (2)
I2	CD7	I4′	107·6 (2)
I2	CD7	O10	85·6 (7)
I4	CD7	I4	90·1 (2)
I4	CD7	O10	175·9 (7)
I4′	CD7	O10	94·1 (7)
I2	CD8	I3	118·1 (2)
I2	CD8	I5	123·5 (2)
I2	CD8	I5′	89·4 (1)
I2	CD8	O10	81·5 (4)
I3	CD8	I5	117·7 (2)
I3	CD8	I5′	93·8 (2)
I3	CD8	O10	89·6 (4)
I5	CD8	I5′	95·0 (1)
I5	CD8	O10	91·0 (5)
I5′	CD8	O10	170·8 (6)
I1	CD9	I3	102·9 (1)
I1	CD9	I6	113·0 (1)
I1	CD9	O11	108·8 (7)
I3	CD9	I6	110·0 (1)
I3	CD9	O11	105·6 (8)
I6	CD9	O11	115·5 (6)

Shorter cadmium–iodine distances were found to prevail in the four membered rings. One of the cadmium–iodine bond lengths with 2·796 Å and 2·727 Å was noticably shorter than the others with 2·974 Å and 3·079 Å, respectively. The single bonded iodine atom Cd-I(6) exhibits the shortest cadmium–iodine distance with 2·696 Å. The cadmium–iodine distances were found to be somewhat shorter in a structurally related four membered ring composed of $(\text{pyridine-N-oxide})_2\text{Cd}_2\text{I}_2$,[13] yet other bond lengths proved to be comparable with those found in **3**.

The structure of **3** is further detailed in an additional perspective drawing in Fig. 7, which revealed yet another though not entirely unexpected feature of

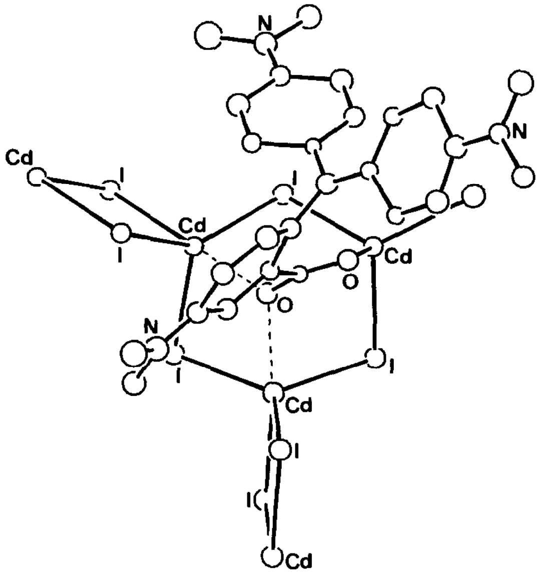


Fig. 7. Perspective drawing of the Cd-I six-membered ring of 3.

the bonding situation of the second oxygen atom belonging to the carboxylate group. It was found to be situated above the cadmium–iodine chair, showing distances to Cd(7) and Cd(8) of 2·42 Å and 2·69 Å, respectively. These distances are larger than other Cd–O distances[21] although significantly smaller than the sum of the Van der Waals radii as found, for example, in the complex of a cadmium(II) maleate dihydrate. Therefore, these cadmium atoms may be considered as five coordinate in the crystalline state, and the environment of the penta-coordinated Cd atoms is decribed best as that of a trigonal bipyramid.

The carbon atoms C(15), C(16), C(22) and C(28) of the triphenylmethyl carbonium unit are all situated in an sp^2-plane. The three phenyl rings are again arranged alternately in a right and a left handed propeller conformation and deviations of the *ortho*-carbon atoms of the phenyl rings to the sp^2-plane are given in Fig. 6.

Some selected angles between the phenyl rings, and the sp^2-plane are displayed in Table 7.

TABLE 7
Selected Angles of Phenyl Rings with the sp^2-Plane of 3

C15, C16, C22, C28	Phenyl C16...C21	33°
C15, C16, C22, C28	Phenyl C22...C27	24°
C15, C16, C22, C28	Phenyl C28...C33	51°
Phenyl C28...C33	Carboxyl C29, C34, C10, O11	27°

A comparison of the values of the distortion angles between the phenyl rings and the sp^2-plane with the corresponding angles of the structure of [CVL·$3ZnI_2$·acetone] indicates that the phenyl rings bearing the carboxylate group are not characterized by any larger twist of angle than the remaining phenyl rings, yet seem solely governed by the requirements of the spatial arrangements in the crystal lattice.

Substituents on the nitrogen atoms are situated in a plane, as indicated by the values of 0·00 and 0·06 Å for the distance of the nitrogen atoms from the plane. The torsion angles between the dimethylamino groups and the respective phenyl rings are found to lie between 0° and 4°. This agrees well with the values found for **2a**, and for comparable data disclosed.[17]

The N-phenyl bond lengths were found to lie between 1·28 and 1·39 Å which might indicate some degree of double bond character, although standard deviations are too large to establish definite values. The packing is ruled by Van der Waals contacts.

One half of a molecule of acetone per monomeric unit is intercalated into the crystal lattice. However, when crystals were heated to 45–50°C in high vacuum, the solvate is removed from the lattice thus causing a collapse of the entire, highly oriented structure, and leaving a product, which, although analyzing for CVL·$3CdI_2$, now exhibits a structure totally amorphous for X-ray studies.

Anhydrous zinc(II)carboxylates, aliphatic or aromatic in nature, have been observed with one, two- or three-dimensional polymeric structures of different types yet displaying a carboxylate moiety symmetrically bound to both oxygen atoms.[22] Zinc crotonate, however, was found[23] to consist of binuclear units with three bridging crotonate ligands $Zn_2(crotonate)_3$ which are connected by a single crotonate link to form a polymeric chain in which only one of the oxygen atoms of the carboxylate group is involved. On the other hand, the X-ray structure analysis of zinc(II)bis-L-pyroglutamate dihydrate showed tetracoordinated zinc atoms surrounded by two L-pyroglutamate anions,[24] each connected through only one of the oxygen atoms of the carboxylate unit, and thus retaining the carboxylate function.

Thus, depending on the nature of the coreactant used, the species responsible for the color formation may exist on the one hand as a singular molecule or, on the other hand, as an intermittently placed substituent attached to a polymer matrix of the metal salt.

Although the X-ray structure determinations of compounds **2a** and **3** show, in the solid state, a definite bonding of the coreactant to the carboxylate group, it may be presumed that in solution dissociation of these complexes will occur to some extent, yet the sp^2-character of the organic moiety is largely retained as indicated by the NMR data of the central carbon atom, and thus the anionic character of the carboxylate group is preserved by solvates of different order.

This somewhat bewildering array of crystal structures establishes the general feasibility of constructing metallic coreactants that bind carboxylate ligands in close proximity in a roughly tetrahedral arrangement that is relatively stable. Many variants of the building matrix are clearly possible and we regard the present examples as prototypes for a potentially extensive and useful series of coreactant species and with a variety of building arrangements for the colorformer upon the given matrix. The presence of intercalated acetone molecules in the crystal lattice is merely a prerequisite to obtain single crystals of a feasible shape for crystallographic determinations, as has been demonstrated for the polymeric crystalline structure of **3**.

The rationale for the formation of **2a** and of **3** involves stable bonds between the carboxylate group and the metallic halides. These bonds lock the geometry of the entire complex, yet they do not seem to determine the formation of monomeric or of polymeric species, at least not on the basis of present knowledge.

The isolation and characterization of these structures of colorforming species will provide a novel entry and sound alternative to the presently existing vague and dubious structural proposals.

Considering the number of lactones and of coreactants reported, it seems apposite to elucidate this method of preparation and gain further insight into the structural intricacies and the mutual effects of the colorforming species which ultimately may lead to new complexes heretofore not accessible by standard techniques.

A forthcoming paper will present an example of the X-ray structure of a fluorane and its coreactant, the second important class of colorformers.

3 EXPERIMENTAL

3.1 Materials and methods

3.1.1 General comments

All melting points were taken in capillary tubes and are uncorrected. ^{13}C NMR spectra were recorded on a Brucker HX-360 NMR spectrometer in the Fourier transform mode with CD_2Cl_2 as solvent. Samples for the infrared spectra were prepared in nujol mulls. The usual preparation of IR specimen in potassium bromide pellets proved sufficient to cause partial decomposition of the organic complexes, about 10–20% of the lactone being detected in the spectra.

6-Dimethylamino-3,3′-bis[4-dimethylamino)phenyl]-1(3H)isobenzofuranone (Crystal Violet lactone) (**1**) was purified by crystallization from ethylene glycolmonomethylether, m.p. 178°C.

Complex ***2a*** (Di-[bis(*p*-dimethylaminophenyl)-(*p*-dimethylaminophenylmethyl-2-carboxylato-O,O′)]bis(μ-iodozinc)μ-iodonium triiodozincate). The complex was prepared by adding 1 (0·825 g, 2 mmol) and zinc iodide (1·54 g, 4·8 mmol) to acetone (14 ml) and allowing to stand for 5 days. Crystals were collected by filtration, and washed with 3 ml of cold acetone, yielding **2a**, 1·19 g (64%), m.p. 218–220°C, dec. IR (cm^{-1}): 1711(w), 1579(vs), 1481(m), 1361(vs), 1172(vs), 941(m), 914(m), 828(m), 792(m).

Analysis calculated for $C_{55}H_{64}I_6N_6O_5Zn_3$: C, 35·77, H, 4·16, I, 41·23, N, 4·55, Zn, 10·61. Found: C, 35·48, H, 3·98, I, 41·35, N, 4·39, Zn, 10·81.

Complex ***2b***. The complex was prepared by adding CVL (1·0 g, 2·4 mmol) and anhydrous zinc bromide (2·7 g, 12 mmol) to 4 ml of acetone. Crystals were collected after standing for 3 days, yielding **2b**, 1·55 g (41%), m.p. 263–268°C dec., IR (cm): 1702(w), 1582(vs), 1468(m), 1362(vs), 1172(vs).

Analysis calculated for $C_{55}H_{64}Br_6N_6O_5Zn_3$: C, 42·22, H, 4·21, Br, 29·98, N, 5·49, Zn, 12·43. Found: C, 42·18, H, 4·21, Br, 29·98, N, 5·32, Zn, 12·74.

Complex ***2c***. The complex was prepared by adding zinc chloride (1·09 g, 8 mmol) to a suspension of CVL 0·83 g, 2 mmol) in 4 ml of acetone. Crystals were collected after standing for 3 days, yielding **2c**, 0·7 g (57%), m.p.

TABLE 8
Crystal Data of **2a** and **3**

Compound	***2a***	***3***
Formula	$C_{52}H_{62}N_6O_4Zn_2I_3^{\oplus}$ $C_3H_6OZnI_3^-$	$\left[\begin{array}{c}C_{26}H_{29}N_3O_2Cd_3I_6\\ \cdot 0{\cdot}5\ \text{Acetone}\end{array}\right]_n$
Crystal size (mm)	0·3 × 0·3 × 0·1	0·6 × 0·4 × 0·2
Crystal system	Triclinic	Monoclinic
Space group	PI	C2/c
a (Å)	15·222 (2)	23·571 (2)
b (Å)	15·368 (2)	16·827 (1)
c (Å)	16·237 (2)	22·812 (2)
α^0	107·29 (2)	
β^0	103·49 (2)	113·94 (2)
γ^0	90·30 (2)	
V (Å^3)	3 515	8 270
Z	2	8
Calcd density (g/cm^3)	1·748	2·479
No. of reflections	7 914	5 429
No. of nonzero reflections	5 735	3 952
No. of parameters	656	380
Final R factor	0·082	0·069

TABLE 9
Positional Parameters of **2a**

Atom	*x*	*y*	*z*	*B* (*A2*)
I1	0·865 2 (2)	0·345 6 (2)	0·122 0 (2)	3·76 (8)
I2	0·864 9 (2)	0·498 3 (2)	−0·065 4 (2)	4·19 (8)
I3	0·674 4 (4)	0·170 3 (2)	0·177 4 (2)	6·8 (1)
I4	0·219 6 (3)	0·388 4 (3)	0·447 1 (3)	7·5 (1)
I5	0·304 3 (4)	0·158 7 (3)	0·269 1 (3)	8·1 (1)
I6	0·440 8 (4)	0·237 4 (4)	0·546 1 (3)	9·8 (2)
Zn7	0·701 3 (4)	0·268 0 (3)	0·083 9 (4)	3·4 (1)
Zn8	0·772 0 (4)	0·405 1 (3)	−0·008 2 (4)	3·0 (1)
Zn9	0·346 0 (6)	0·284 5 (5)	0·416 4 (5)	7·5 (2)
O10	0·722 (2)	0·290 (2)	−0·107 (2)	2·7 (7)
O11	0·674 (2)	0·197 (2)	−0·039 (2)	3·3 (7)
O12	0·625 (2)	0·370 (2)	0·096 (2)	3·4 (8)
O13	0·670 (2)	0·465 (2)	0·037 (2)	3·8 (8)
N14	0·437 (3)	0·009 (3)	−0·310 (3)	5 (1)
N15	1·052 (3)	0·188 (2)	0·071 (3)	4 (1)
N16	0·886 (3)	0·279 (3)	−0·524 (3)	6 (1)
N17	0·363 (3)	0·498 (3)	0·217 (3)	5(1)
N18	0·995 (2)	0·544 (2)	0·324 (2)	3·4 (9)
N19	0·656 (3)	0·922 (3)	−0·026 (3)	5 (1)
C20	0·797 (3)	0·161 (3)	−0·249 (3)	3 (1)
C21	0·704 (3)	0·130 (3)	−0·263 (3)	3 (1)
C22	0·658 (3)	0·147 (3)	−0·194 (3)	4 (1)
C23	0·564 (3)	0·109 (3)	−0·212 (3)	4 (1)
C24	0·527 (3)	0·047 (3)	−0·296 (3)	4 (1)
C25	0·572 (3)	0·026 (3)	−0·365 (3)	4 (1)
C26	0·658 (3)	0·068 (3)	−0·348 (3)	3 (1)
C27	0·687 (3)	0·216 (3)	−0·102 (3)	4 (1)
C28	0·380 (3)	0·042 (3)	−0·246 (3)	5 (1)
C29	0·400 (5)	−0·055 (5)	−0·394 (4)	8 (2)
C30	0·861 (3)	0·168 (2)	−0·168 (3)	2 (1)
C31	0·852 (3)	0·110 (3)	−0·122 (3)	3 (1)
C32	0·915 (3)	0·114 (3)	−0·046 (3)	3 (1)
C33	0·987 (3)	0·181 (3)	−0·011 (3)	4 (1)
C34	0·997 (3)	0·241 (3)	−0·060 (3)	3 (1)
C35	0·936 (3)	0·238 (3)	−0·138 (3)	3 (1)
C36	1·027 (4)	0·138 (3)	0·129 (4)	5 (2)
C37	1·124 (3)	0·260 (3)	0·101 (3)	4 (1)
C38	0·817 (3)	0·196 (3)	−0·318 (3)	3 (1)
C39	0·910 (3)	0·191 (3)	−0·330 (3)	4 (1)
C40	0·932 (4)	0·218 (3)	−0·401 (3)	5 (1)
C41	0·863 (3)	0·254 (3)	−0·452 (3)	5 (1)
C42	0·772 (3)	0·255 (3)	−0·445 (3)	4 (1)
C43	0·750 (3)	0·229 (3)	−0·379 (3)	4 (1)
C44	0·820 (4)	0·319 (3)	−0·583 (3)	5 (1)

(*continued*)

TABLE 9—*contd.*

Atom	*x*	*y*	*z*	*B (A2)*
C45	0·981 (4)	0·277 (4)	−0·530 (4)	7 (2)
C46	0·670 (3)	0·650 (3)	0·148 (3)	3 (1)
C47	0·585 (3)	0·608 (3)	0·150 (3)	4 (1)
C48	0·566 (3)	0·513 (2)	0·128 (2)	1·8 (9)
C49	0·492 (3)	0·475 (3)	0·144 (3)	3 (1)
C50	0·436 (3)	0·529 (3)	0·189 (3)	4 (1)
C51	0·448 (3)	0·627 (3)	0·209 (3)	4 (1)
C52	0·523 (3)	0·661 (3)	0·186 (3)	3 (1)
C53	0·618 (3)	0·448 (3)	0·080 (3)	4 (1)
C54	0·318 (4)	0·556 (4)	0·285 (3)	5 (2)
C55	0·345 (3)	0·395 (3)	0·188 (3)	4 (1)
C56	0·753 (3)	0·626 (2)	0·190 (3)	2 (1)
C57	0·830 (3)	0·627 (3)	0·158 (3)	3 (1)
C58	0·913 (3)	0·604 (3)	0·207 (3)	3 (1)
C59	0·913 (3)	0·570 (3)	0·282 (3)	3 (1)
C60	0·829 (3)	0·572 (3)	0·307 (3)	3 (1)
C61	0·753 (3)	0·594 (2)	0·265 (3)	2 (1)
C62	0·992 (4)	0·501 (4)	0·392 (4)	6 (2)
C63	1·076 (3)	0·540 (3)	0·291 (3)	3 (1)
C64	0·660 (3)	0·721 (2)	0·104 (3)	2 (1)
C65	0·584 (3)	0·734 (3)	0·043 (3)	4 (1)
C66	0·581 (3)	0·800 (3)	0·001 (3)	4 (1)
C67	0·657 (3)	0·857 (3)	0·019 (3)	4 (1)
C68	0·736 (3)	0·853 (3)	0·078 (3)	3 (1)
C69	0·739 (3)	0·784 (3)	0·123 (3)	3 (1)
C70	0·575 (4)	0·939 (4)	−0·084 (4)	6 (2)
C71	0·743 (3)	0·979 (3)	−0·011 (3)	5 (1)
O72	0·430 (3)	0·385 (3)	0·398 (3)	9(1)*
C73	0·509 (6)	0·388 (6)	0·389 (6)	12 (3)*
C74	0·565 (7)	0·459 (7)	0·369 (7)	15 (3)*
C75	0·559 (8)	0·306 (8)	0·381 (8)	17 (4)*

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2 * B(1,1) + b2 * B(2,2) + c^2 * B(3,3) + ab(cos gamma) * B(1,2) + ac(cos beta) * B(1,3) + bc(cos alpha) * B(2,3)].

260–265°C dec. IR (cm^{-1}): 1583(vs), 1465(s), 1365(vs), 1172(vs), 943(m), 915(m), 830(m), 794(m).

Analysis calculated for $C_{55}H_{64}Cl_6N_6O_5Zn_3$: C, 50·90, H, 4·97, Cl, 16·39, N, 6·48, Zn, 15·11. Found: C, 50·91, H, 5·02, Cl, 16·74, N, 6·53, Zn, 15·70.

Complex 3. The complex was prepared by adding CVL (0·42 g, 1 mmol) to a solution of cadmium iodide (0·366 g, 1 mmol) in 12 ml of acetone. Crystals

TABLE 10
Positional Parameters of **3**

Atom	*x*	*y*	*z*	*B* (*A2*)
I1	0·678 2 (1)	0·071 3 (2)	0·642 4 (2)	4·82 (8)
I2	0·633 9 (1)	−0·067 9 (2)	0·454 9 (1)	5·37 (8)
I3	0·824 2 (1)	−0·092 5 (2)	0·639 5 (2)	5·30 (8)
I4	0·520 6 (1)	0·111 3 (2)	0·478 8 (1)	4·45 (7)
I5	0·710 6 (1)	−0·325 1 (2)	0·549 6 (2)	5·69 (8)
I6	0·837 3 (2)	−0·003 5 (3)	0·832 2 (2)	7·3 (1)
CD7	0·590 9 (1)	−0·029 8 (2)	0·550 3 (2)	4·03 (8)
CD8	0·7237 (2)	−0·164 8 (2)	0·542 5 (2)	5·3 (1)
CD9	0·757 8 (1)	−0·051 4 (2)	0·714 8 (2)	4·51 (8)
O10	0·655 (1)	−0·139 (2)	0·610 (1)	3·5 (6)
O11	0·702 (1)	−0·156 (2)	0·713 (1)	4·5 (7)
N12	0·579 (2)	0·139 (2)	0·732 (2)	6 (1)
N13	0·691 (1)	−0·341 (2)	1·010 (1)	4·2 (9)
N14	0·503 (2)	−0·361 (2)	0·536 (2)	5 (1)
C15	0·614 (2)	−0·193 (3)	0·769 (2)	4 (1)
C16	0·605 (2)	−0·108 (2)	0·761 (2)	4 (1)
C17	0·645 (2)	−0·050 (3)	0·805 (2)	4 (1)
C18	0·640 (2)	0·034 (3)	0·797 (2)	5 (1)
C19	0·589 (2)	0·062 (3)	0·742 (2)	4 (1)
C20	0·546 (2)	0·002 (3)	0·697 (2)	4 (1)
C21	0·554 (2)	−0·077 (3)	0·705 (2)	4 (1)
C22	0·636 (2)	−0·225 (3)	0·830 (2)	4 (1)
C23	0·630 (2)	−0·190 (3)	0·883 (2)	5 (1)
C24	0·648 (2)	−0·226 (3)	0·944 (2)	5 (1)
C25	0·673 (2)	−0·305 (3)	0·950 (2)	5 (1)
C26	0·680 (2)	−0·344 (3)	0·896 (2)	5 (1)
C27	0·659 (2)	−0·310 (3)	0·839 (2)	4 (1)
C28	0·592 (2)	−0·240 (3)	0·711 (2)	4 (1)
C29	0·609 (2)	−0·227 (3)	0·657 (2)	4 (1)
C30	0·580 (2)	−0·268 (2)	0·600 (2)	3 (1)
C31	0·532 (2)	−0·328 (2)	0·591 (2)	4 (1)
C32	0·520 (2)	−0·345 (3)	0·649 (2)	5 (1)
C33	0·553 (2)	−0·306 (3)	0·706 (2)	5 (1)
C34	0·659 (2)	−0·168 (2)	0·658 (2)	2·9 (9)
C35	0·527 (3)	0·170 (4)	0·673 (3)	8 (2)
C36	0·623 (3)	0·195 (4)	0·778 (3)	8 (2)
C37	0·687 (2)	−0·302 (3)	1·061 (2)	7 (2)
C38	0·714 (2)	−0·426 (3)	1·022 (2)	5 (1)
C39	0·514 (2)	−0·342 (3)	0·478 (2)	6 (1)
C40	0·461 (2)	−0·430 (3)	0·528 (2)	7 (2)
O41	0·500	0·335 (5)	0·750	13 (3)
C42	0·500	0·412 (6)	0·750	9 (3)
C43	0·508 (4)	0·431 (6)	0·694 (4)	16 (4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a2*B(1, 1) + b2*B(2, 2) + c^2*B(3, 3) + ab(cos gamma)*B(1, 2) + ac(cos beta)*B(1, 3) + bc(cos alpha)*B(2, 3)].

were collected after 2 days by filtration, and washed with 3 ml of acetone, yielding **3**, 0·65 g (41%), m.p. 233–237°C dec. IR (cm^{-1}): 1702(w), 1582(vs), 1468(m), 1362(vs), 1172(vs).

Analysis calculated for: $C_{55}H_{64}N_6O_5I_{12}Cd_6$: C, 21·40, H, 2·09, N, 2·72, I 49·34, Cd, 21·85. Found: C, 21·89, H, 2·28, N, 2·80, I 48·74, Cd, 21·37.

X-ray analyses of ***2a*** *and* ***3***. Crystal data and specifics for each data set for both compounds are given in Table 8. Intensity measurements were made on a Philips PW 1100 automatic diffractometer with monochromated MoKα radiation. Data reduction included corrections for background, Lorentz polarization and absorption, the latter based upon ψ-scans of reflections near $\chi = 90°$, by using the program EAC of the Enraf-Nonius SDP programs.[25] Reflections having $I > 2\sigma(I)$ were considered observed and used in the refinements. The structures were solved by direct methods (SDP MULTAN 80).[26] Full matrix least squares refinements were carried out with the anisotropic thermal parameters for all atoms except those of acetone in both structures; hydrogen atoms could not be localized. Final fractional coordinates with their standard deviations are given in Tables 9 and 10.

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