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Interaction of Colorformers and Coreactants. Part II. Crystal Structure of a Xanthene Type Colorformer and Cadmium Iodide

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ABSTRACT

A crystalline adduct composed of a xanthene moiety representing the colorformer and cadmium iodide as the coreactant has been synthesized. Single crystals of the composition $C_{56}H_{46}N_2O_6 . Cd_2I_4 .$ *acetone were obtained as acetone solvate.* ^{13}*C-NMR, X-ray and crystallographic data have been collected for this complex. Two xanthene parts are linked via their carboxylate groups to a four-membered ring composed of a* Cd_2I_4 *unit. Interatomic distances indicate that the molecule possesses a quinone-like structure, with the phenyl ring bearing the carboxylate group standing nearly at right angles to the xanthene part. Intercalated acetone molecules are a prerequisite for the formation of single crystals.*

1 INTRODUCTION

The structures of reaction products which are applied in carbonless imaging systems have been elucidated, and models have been presented in the previous paper.[1] These structures, however, were confined to those involving substituted triphenylmethyl carbonium ions such as were formed from Crystal Violet Lactone and appropriate metal salts as coreactants.

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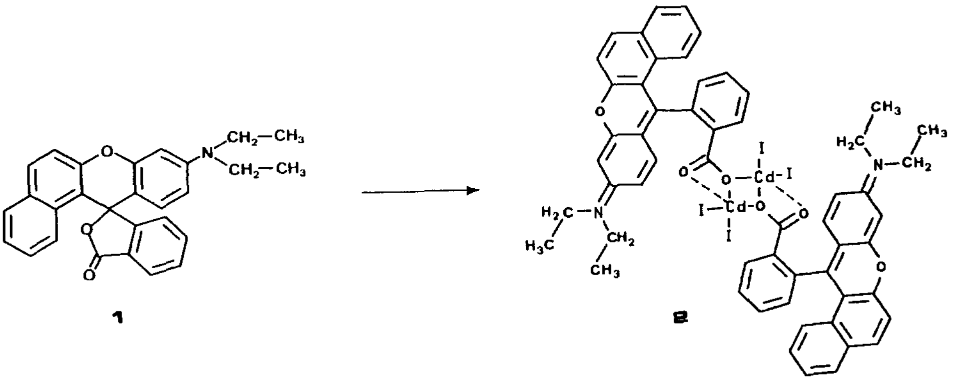


Scheme 1

Recent years have witnessed in the patent literature a proliferation of substituted aminofluorane type compounds which gave rise to a wide spectrum of multicolored blends of colorformers. In particular, since the design of a uniformly impure and black dye targeted on the synthesis of 3-dialkylaminofluoranes, we have endeavoured to elucidate structural requirements for compounds composed of a fluorane and a metallic coreactant.

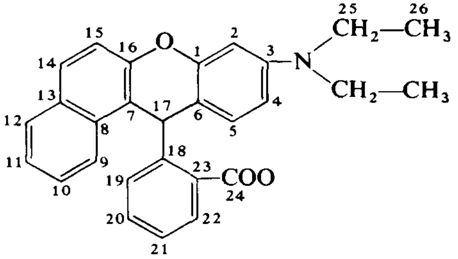
Previous work had focused on the preparation of single crystals of addition compounds comprising triphenylmethyl carbonium ions with carboxylate moieties attached, and zinc or cadmium iodides as coreactants. It was found that acetone molecules, either intercalated in the crystal lattice or bound as a part of an anion such as $[ZnI_3 \text{ acetone}]^{\ominus}$, were a prerequisite for the formation of single crystals feasible for an X-ray determination of their molecular structure.

We present an example of a fluorane derivative with cadmium iodide as coreactant, this presenting the unique possibility to study the conformational requirements and predictions of a 3-dialkylamino-substituted fluorane derivative with a coreactant attached to the carboxylate moiety. Both compounds undergo rapid reaction, yielding large orange to red colored crystals.

2 RESULTS AND DISCUSSION

The reaction of **1** and cadmium iodide in acetone solution proved especially rewarding because of the excellent crystallinity of the orange colored platelets formed. Although many crystals were interspersed again with large aggregates and were non-transparent, some of them were found suitable for X-ray work.

TABLE 1
^{13}C-NMR Data of **2**



^{13}C-NMR δ 172·20 (C-24), 162·25 (C-17), 158·28, 157·61, 157·23 (C-1, C-3, C-16), 141·11 (C-14), 134·05, 132·89, 131·91, 130·76, 130·64, 129·51, 128·47, 127·41, 126·18, 118·82, 118·46 (C-4, C-5, C-9, C-10, C-11, C-12, C-15, C-19, C-20, C-21, C-22), 96·25 (C-2), 47·25, 47·04 (C-25), 13·75, 12·46 (C-26).

The reaction of cadmium iodide and **1** using acetone as solvent led to the formation of **2**, having the analytical composition of $C_{56}H_{46}N_2O_6 . Cd_2I_4 . C_3H_6O$. Extensive disintegration in dilute solution was noticed, as judged by the gradual disappearance of the red color in solutions, which precluded measurements of extinction coefficients and molecular weight determinations.

2.1 IR and ^{13}C-NMR results

The IR spectra of **2** showed one rather weak frequency for the intercalated acetone molecule at 1708 cm^{-1}. The strong band assigned to the lactone frequency at 1763 cm^{-1} was absent. There are several strong bands which are associated with the absorption frequencies of the aromatic part of the molecule.

The ^{13}C-NMR spectrum was recorded in a solution in deuteromethylene chloride. The results are detailed in Table 1. They show a value of $\delta = 162{\cdot}25$ ppm for the central sp^2 carbon atom. The two signals at 47·25 and 47·04 ppm, and at 13·75 and 12·46 ppm for C(25) and C(26) respectively, indicated non-equivalency of the two ethyl groups attached to the nitrogen atom, and thus further confirming the quinone structure of the molecule which is clearly borne out from the X-ray structural data.

2.2 Solid-state structure of 2

The results of the X-ray diffraction studies are illustrated in Figs 1–4. Selected interatomic distances and bond angles are shown in Tables 2 and 3 respectively.

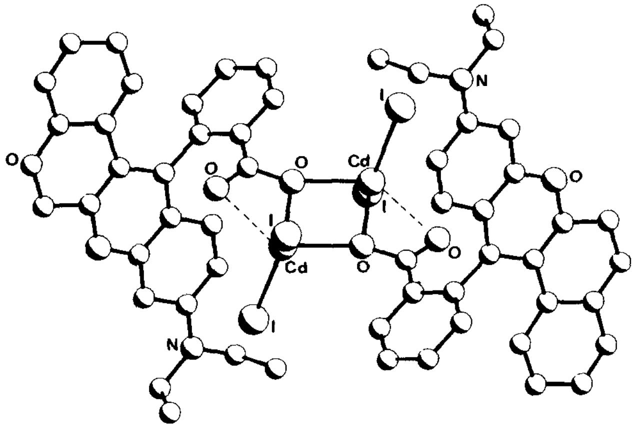


Fig. 1. Perspective drawing of the molecular structure of **2**.

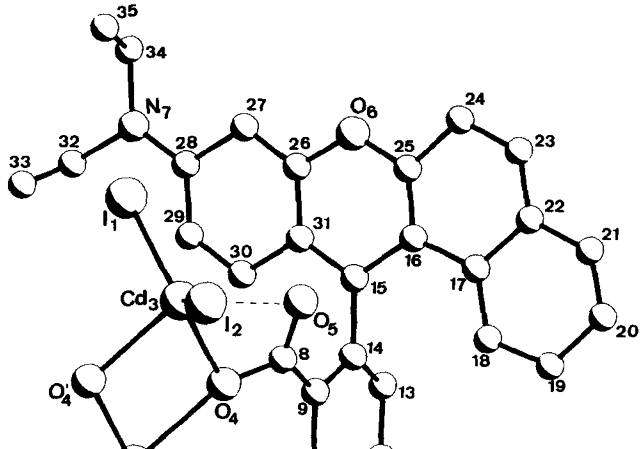


Fig. 2. Atom numbering of **2**.

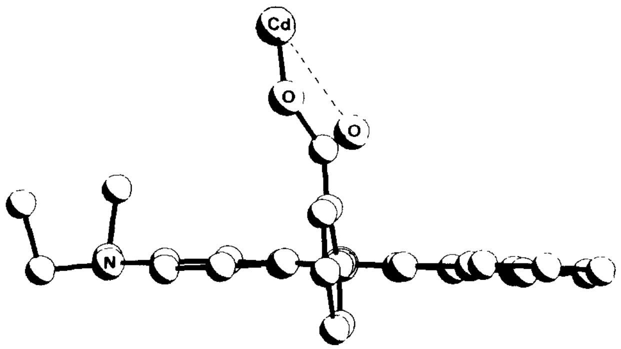


Fig. 3. Side view of **2**.

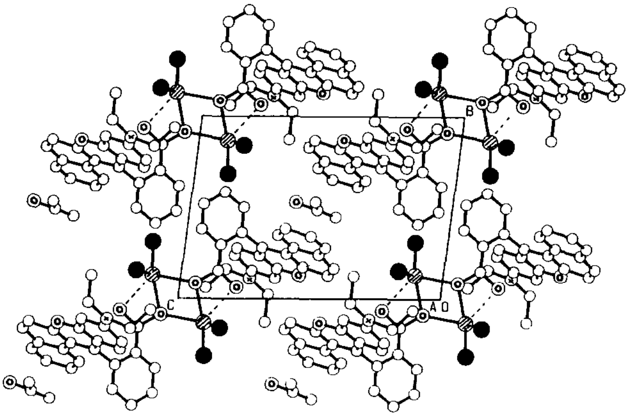


Fig. 4. Packing diagram of **2**.

TABLE 2
Selected Bond Lengths of **2**

Atom 1	*Atom 2*	*Distance*	*Atom 1*	*Atom 2*	*Distance*
I1	Cd3	2·727 (4)	O4	C8	1·38 (4)
I2	Cd3	2·671 (4)	O5	C8	1·29 (3)
Cd3	Cd3	3·704 (3)	O6	C25	1·35 (3)
Cd3	O4	2·21 (2)	O6	C26	1·37 (3)
Cd3	O4	2·39 (2)	N7	C28	1·38 (4)
Cd3	O5	2·66 (2)	N7	C32	1·56 (5)
			N7	C34	1·49 (3)
			C8	C9	1·42 (4)

TABLE 3
Selected Bond Angles of **2**

Atom 1	*Atom 2*	*Atom 3*	*Angle* (°)	*Atom 1*	*Atom 2*	*Atom 3*	*Angle* (°)
I1	Cd3	I2	130·3 (1)	Cd3	O4	Cd3′	107·5 (8)
I1	Cd3	O4	111·9 (6)	Cd3	O4	C8	107·0 (1)
I1	Cd3	O4′	95·3 (6)	Cd3	O4′	C8	140·0 (2)
I1	Cd3	O5	94·5 (5)	Cd3	O5	C8	89·0 (2)
I2	Cd3	O4	116·8 (7)	C25	O6	C26	120·0 (2)
I2	Cd3	O4′	107·8 (7)	C28	N7	C32	119·0 (2)
I2	Cd3	O5	107·0 (6)	C28	N7	C34	124·0 (3)
O4	Cd3	O4′	72·5 (6)	C32	N7	C34	117·0 (2)
O4	Cd3	O5	52·4 (6)				
O4′	Cd3	O5	123·6 (5)				

The molecular structure of **2** is presented in Fig. 1. The compound contains two 9-phenylxanthyl groups which are linked via their carboxylate unit to the cadmium atoms which form the central part, composed of a Cd_2I_4 moiety as the center of symmetry.

Each cadmium atom is pentavalently coordinated, and each is bonded to two iodine atoms and three oxygen atoms, thus recalling the bonding situation in the compound formed from Crystal Violet Lactone and cadmium iodide.[1] The atom numbering is shown in Fig. 2.

The two Cd–I bond lengths of 2·671 and 2·727 Å are within the expected range for these bonds. Previously, the Cd–I distance to a singly coordinated iodine atom, as in [CVL . $3CdI_2$. acetone], was found to be 2·696 Å,[1] and in another compound 2·72 Å,[2] whereas in the Cd_2I_4 anion the distances of the corresponding singly bonded iodine atoms were 2·693 and 2·704 Å respectively.[3]

The structure reveals also three distinctly different Cd–O bond lengths of 2·21, 2·39 and 2·66 Å, yet the highest value of 2·66 Å is still significantly smaller than the sum of their van der Waals radii.

Four-membered rings consisting of cadmium and of oxygen atoms have been reported previously in several instances. For example, the Cd–O distances in cadmium oxydiacetate trihydrate[4] are reported to be 2·345 and 2·492 Å. Carboxylic acid groups known to be linked with cadmium atoms have been found in tetrakis(salicylato)tetraaquodicadmium(II),[5] having Cd–O distances of 2·291 and 2·530 Å respectively.

A side view of the organic part of **2** is shown in Fig. 3. The xanthene part of the molecule is planar, with the atoms C(18)–C(21), N(7), C(32) and C(34) lying in this plane. The remaining phenyl ring C(9)–C(14) stands nearly at right angles to the xanthene part, the large dihedral angle of 97° caused by the exigencies of the naphthalene part and the exocyclic carboxylate group with the adherent cadmium iodide counterpart. The carboxylate moiety is twisted out of the plane of the phenyl ring by 30°. A similar conformation was also found in a rhodamine tetrachloroplatinate(II) salt,[6] its angles being 93° and 10° respectively.

Although standard deviations between the light atoms are rather large, the atomic distances, viz. C(15)–C(31) with 1·39 Å, C(29)–C(3) with 1·37 Å, C(26)–C(27) with 1·35 Å and C(28)–N(7) with 1·38 Å, indicate that the correct structure of **2** must be represented by that of a quinone type with N(7) being hybridized, as depicted in Formula 2 (Scheme 1).

The molecular packing is shown in Fig. 4. The unit cell contains one $[C_{56}H_{46}N_2O_6 . Cd_2I_4]$ complex, and again, as noted previously, one disordered molecule of acetone was interspersed in the crystal lattice. There are no short atomic distances between the metal complexes.

2.3 Conclusions

The first example of a colorformer with a cationic xanthene structure is shown to be stabilized in a quinoid form. The phenyl ring bearing the carboxylate group stands nearly at right angles to the xanthene part.

Each colorformer investigated thus far has shown a different structural moiety and bonding situation, embedded in a matrix of the attached coreactant.

Generally, vague structural proposals have been attempted and tentatively put forward in the past 20 years, yet the true intricacies of the structural interactions showed in reality a healthy disrespect for rationalizations on a structural basis which, on the other hand, turned their chemistry into a well known colorama.

3 EXPERIMENTAL

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 infrared spectra were prepared in nujol mulls.

TABLE 4
Crystal Data

Compound	**2**
Formula	$C_{56}H_{46}N_2O_6 . Cd_2I_4 . C_3H_6O$
Crystal size (mm)	0·8 × 0·15 × 0·05
Crystal system	Triclinic
Space group	PI
a (Å)	10·934 (1)
b (Å)	11·048 (1)
c (Å)	13·912 (2)
α (°)	95·47 (2)
β (°)	92·00 (2)
γ (°)	117·72 (2)
V (Å^3)	1 475
Z	1
Calculation density (g/cm^3)	1·876
Number of reflections	4 766
Number of nonzero reflections	2 771
Number of parameters	352
Final *R* factor	0·072

TABLE 5

Table of Positional Parameters

Atom	*x*	*y*	*z*	*B (A2)*
I1	1·3148 (2)	1·1570 (3)	0·1729 (2)	6·09 (7)
I2	0·9668 (3)	1·3125 (3)	0·1256 (3)	9·28 (8)
Cd3	1·0642 (2)	1·1309 (2)	0·1085 (2)	3·82 (5)
O4	0·912 (2)	0·914 (2)	0·059 (1)	4·3 (6)
O5	0·920 (2)	0·935 (2)	0·217 (1)	3·7 (5)
O6	1·140 (2)	0·868 (2)	0·449 (1)	3·0 (5)
N7	1·499 (2)	0·886 (2)	0·263 (2)	3·8 (7)
C8	0·880 (2)	0·847 (3)	0·140 (2)	3·2 (7)
C9	0·810 (2)	0·702 (2)	0·135 (2)	2·5 (7)
C10	0·715 (2)	0·618 (3)	0·055 (2)	2·9 (7)
C11	0·650 (3)	0·479 (3)	0·051 (2)	3·7 (8)
C12	0·674 (3)	0·412 (3)	0·125 (2)	3·1 (7)
C13	0·769 (2)	0·496 (3)	0·205 (2)	2·9 (7)
C14	0·829 (2)	0·635 (2)	0·209 (2)	2·1 (6)
C15	0·934 (2)	0·719 (2)	0·294 (2)	2·6 (7)
C16	0·897 (2)	0·754 (2)	0·390 (2)	2·2 (6)
C17	0·754 (3)	0·721 (3)	0·412 (2)	3·3 (8)
C18	0·635 (3)	0·651 (3)	0·348 (2)	3·9 (8)
C19	0·499 (3)	0·615 (3)	0·373 (2)	4·4 (9)
C20	0·484 (3)	0·657 (3)	0·474 (2)	4·6 (9)
C21	0·599 (3)	0·721 (3)	0·534 (2)	4·1 (9)
C22	0·739 (3)	0·758 (3)	0·513 (2)	3·3 (8)
C23	0·853 (3)	0·834 (3)	0·579 (2)	3·8 (8)
C24	0·989 (3)	0·871 (3)	0·560 (2)	3·8 (8)
C25	1·004 (2)	0·826 (3)	0·460 (2)	3·1 (7)
C26	1·180 (2)	0·835 (2)	0·363 (2)	2·4 (7)
C27	1·318 (3)	0·886 (3)	0·359 (2)	2·7 (7)
C28	1·360 (3)	0·846 (3)	0·268 (2)	3·4 (8)
C29	1·259 (2)	0·761 (3)	0·194 (2)	2·9 (7)
C30	1·121 (3)	0·722 (3)	0·198 (2)	3·5 (8)
C31	1·075 (2)	0·763 (2)	0·288 (2)	2·4 (7)
C32	0·546 (3)	0·838 (3)	0·169 (3)	5 (1)
C33	0·565 (3)	0·938 (4)	0·099 (3)	6 (1)
C34	1·610 (3)	0·977 (3)	0·341 (2)	4·1 (9)
C35	0·646 (3)	0·126 (3)	0·342 (3)	4·6 (9)
O36	0·942 (3)	0·531 (3)	0·600 (3)	13 (1)
C37	0·845 (3)	0·451 (3)	0·443 (2)	5·0 (9)
C38	0·937 (3)	0·486 (3)	0·510 (3)	4·9 (9)
C39	1·107 (9)	0·54 (1)	0·533 (9)	36 (5)

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) + c2 * B(3,3) + ab(cos gamma) * B(1,2)
+ ac(cos beta) * B(1,3) + bc(cos alpha) * B(2,3)].

9-(Diethylamino)-spiro[12H-benzo[a]xanthene-12,1'(3H)-isobenzofuran]-3'-one (**1**) was obtained from commercial sources and purified by crystallization from ethylene glycol monoethylether, m.p. 220–222°C.[7]

Complex **2** (Bis[9-(diethylamino)xanthene-12-phenyl-2'-carboxylato-O,O']tetraiodocadmate). The complex was prepared by adding **1** (0·21 g, 5 mmol) to a solution of cadmium iodide (0·5 g, 4·4 mmol) in acetone (35 ml) and allowing it to stand for 10 h at ambient temperature. Crystals were collected by filtration and washed with cold acetone (4 ml), yielding red crystals of **2**, 0·32 g (51%), m.p. 190–193°C dec. IR cm^{-1}: 1714 (w), 1631 (m), 1509 (m), 1465 (vs), 1377 (vs).

Analysis calculated for $C_{56}H_{46}N_2O_6 . Cd_2I_4 . C_3H_6O$: C, 43·46; H, 3·03; I, 31·13; N, 1·76; Cd, 13·79. Found: C, 43·65; H, 3·31; I, 31·09; N, 1·80; Cd, 13·82.

X-ray analysis of **2**. Crystal data of **2** are given in Table 4. Intensity measurements were made on a Philips PW 1100 automatic diffractometer with monochromated MoKα radiation at a temperature of 1503 K. Reflections having $I > 2\sigma(2)$ were considered observed and used in the refinements. The structures were solved by direct methods (SDP MULTAN 80).[8] Full matrix least square refinements were carried out with anisotropic thermal parameters for all the atoms. Hydrogen atoms could not be located. Final coordinates with their standard deviations are given in Table 5.

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