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Photoluminescent Enhancement of Ninhydrin Developed Fingerprints by Metal Complexation: Structural Studies of Complexes Formed Between Ruhemann's Purple and Group IIb Metal Salts

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ABSTRACT: Ruhemann's purple (RP), formed in the ninhydrin development of latent fingerprints, readily coordinates to a number of metal cations. The luminescent behavior of the Group IIb complexes has been used in the enhancement of fingerprints developed with ninhydrin. Spectroscopic evidence is presented which indicates that all three complexes have similar structures. The structure of the cadmium complex has been determined by X-ray diffraction and found to contain a 1 : 1 ratio of metal to chelating agent (RP). The properties of this complex suggest that it is the active agent in the cadmium(II) promoted photoluminescence of ninhydrin developed fingerprints. Coordinated water in the complex explains the need for moisture in the enhancement procedure.

KEYWORDS: criminalistics, fingerprints, Ruhemann's purple, cadmium, ninhydrin, cadmium complexes, IIb metal complexes, photoluminescence, X-ray diffraction

The development of latent fingerprints on paper surfaces using ninhydrin as the colorimetric reagent is a widely used technique in operational crime laboratories. The chromogen in this technique is Ruhemann's purple (RP) [Fig. 1 (1)], which is formed from the reaction between ninhydrin and the amino acids present in the fingerprint deposit. RP is an active chelating agent and forms colored coordination complexes with a variety of metals [1,2].

The ability of RP to complex readily with certain metal cations has been exploited for the spectrophotometric determination of lead, mercury, and bismuth ions [3,4]. More recently, new analytical methods have been developed which use the photoluminescent properties of a number of these metal complexes. In particular, the Group IIb transition metal complexes show favorable luminescent properties at low temperature (77K) and considerable enhance-

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ment of ninhydrin treated fingerprints can be achieved [5]. The luminescent properties of RP-metal complexes (particularly the zinc (II) complex) were first recognized by Herod and Menzel in 1982 and applied in the area of latent fingerprint detection [6].

Kawerau and Wieland [1] used the stability of these complexes for the conservation of amino acid chromatograms. They found that ninhydrin developed amino acid spots on paper chromatograms rapidly lost their "blue" coloration. However, metal complexation [Zn(II), Cd(II), Co(II), or Cu(II)] changed the coloration from "blue" to red and rendered the amino acid spots "a great deal more stable." Wieland [7] proposed the structure [Fig. 1 (2)] for the RP-metal complex where the metal is bound between two molecules of RP (giving a RP-metal ratio of 2:1). He based this structure on unpublished observations. The same formulation has been reported in 1985 by Menzel and Almog [8]. In neither case was evidence provided to support this structure [Fig. 1 (2)].

Burkina [3], Kanke [4], and their co-workers gave evidence to suggest that the complex formed between RP and Hg(II) had a RP-metal ratio of 2:1. In contrast to this, Fritz and Swinehart [9] determined that the corresponding Ni(II) complex had a RP-metal ratio of 1:1. Despite these observations, a definite structure for a RP-metal complex has never been reported.

We have now isolated a cadmium(II) complex of RP which was shown by X-ray diffraction to have structure (3; $M = \text{Cd}$, $X = \text{I}$) (Fig. 2). This indicates that the earlier formulations were incorrect as the complex contains only a single chelating molecule of RP. Spectral evidence is presented to support similar structures for the zinc(II) and mercury(II) complexes.

Materials

All chemicals were of analytical grade, used without further purification. Spectrophotometric data were obtained on a Cary 219 Spectrophotometer (Varian, USA). X-Ray data were collected by Dr. W. T. Robinson at the University of Canterbury, Christchurch, New Zealand, using a Nicolet R3m diffractometer (MoK α radiation) (Nicolet, USA).

Job's Method Analyses of the Complexes

RP (1) was prepared as the sodium salt by heating ninhydrin with glycine in a citrate buffer (pH 5) according to the method of Moore and Stein [10]. The absorption spectrum of RP in ethanol showed two peaks in the visible region, at 408 ($\epsilon = 22\ 400$) and 575 nm ($\epsilon =$

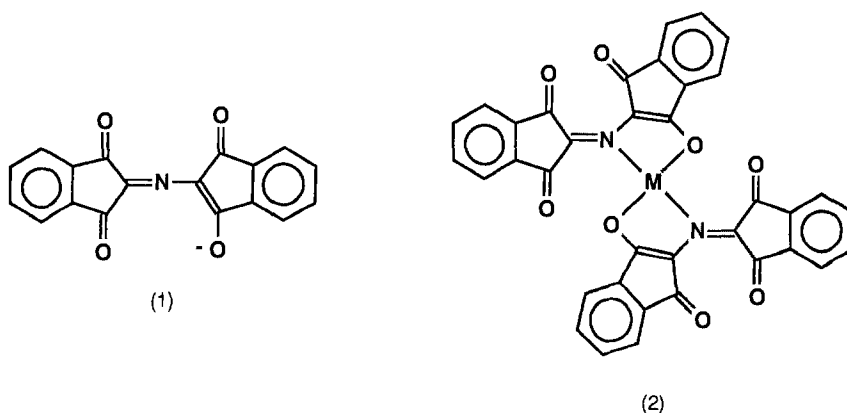


FIG. 1—(1) *Ruhemann's purple* and (2) *previously proposed RP-metal complex structure*.

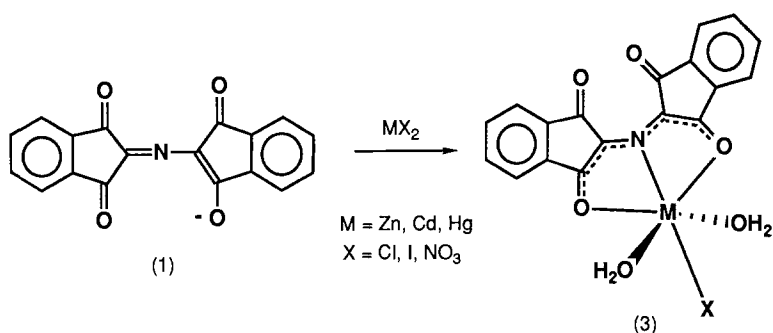
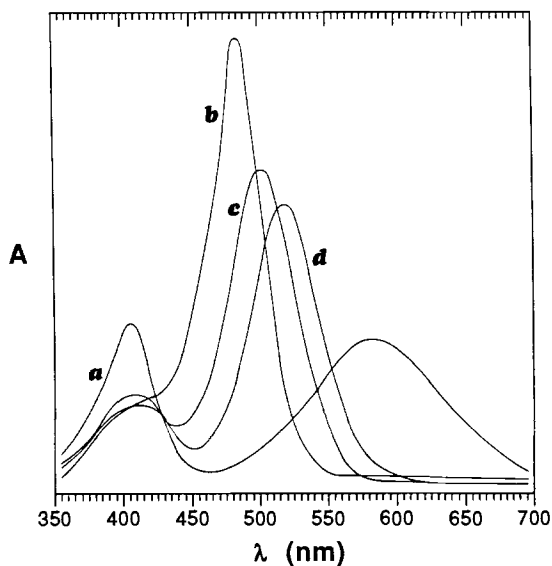


FIG. 2.—Formation of RP-metal complexes.

FIG. 3.—Visible absorption spectra of (a) RP, and its complexes with (b) ZnI_2 , (c) CdI_2 , and (d) HgCl_2 , recorded in ethanol solution.

20 000). Addition of a Zn(II), Cd(II), or Hg(II) salt to an ethanolic solution of RP resulted in one major peak in the visible absorption spectrum (Fig. 3). Each complex in solution was analyzed by Job's method [11] according to Vosburgh [12].

Zinc (II) Complex

Equimolar ($3.0 \times 10^{-5}M$) solutions of RP and zinc iodide (ZnI_2) in ethanol were prepared. These solutions were mixed in varying proportions and the absorbance of each of the resulting solutions measured at two different wavelengths (Table 1). The absolute difference $|Y|$ between the observed absorbance of each solution and that expected for no reaction, was plotted against X , the volume (mL) of Zn(II) solution added to $(50 - X)$ mL of RP solution (Fig. 4).

TABLE 1—Absorbance data and calculated values for the Job's method analysis of the complex formed between RP and ZnI_2 .

X, ^a mL	Abs. at 485 nm			Abs. at 580 nm		
	Obs.	Calc. ^b	Y ^c	Obs.	Calc. ^b	Y ^c
0	0.096	0.096	0.000	0.590	0.590	0.000
10	0.415	0.077	0.338	0.343	0.472	0.129
15	0.544	0.067	0.477	0.239	0.413	0.174
20	0.688	0.058	0.630	0.132	0.354	0.222
25	0.780	0.048	0.732	0.040	0.295	0.255
30	0.685	0.039	0.646	0.011	0.236	0.225
35	0.518	0.029	0.490	0.007	0.177	0.164
40	0.349	0.019	0.330	0.004	0.118	0.114
50	0.000	0.000	0.000	0.000	0.000	0.000

^aVolume (mL) of metal salt solution added to (50 - X) mL of RP solution.

^bCalculated absorbance assuming no reaction.

^cAbsolute value of the difference between observed and calculated values.

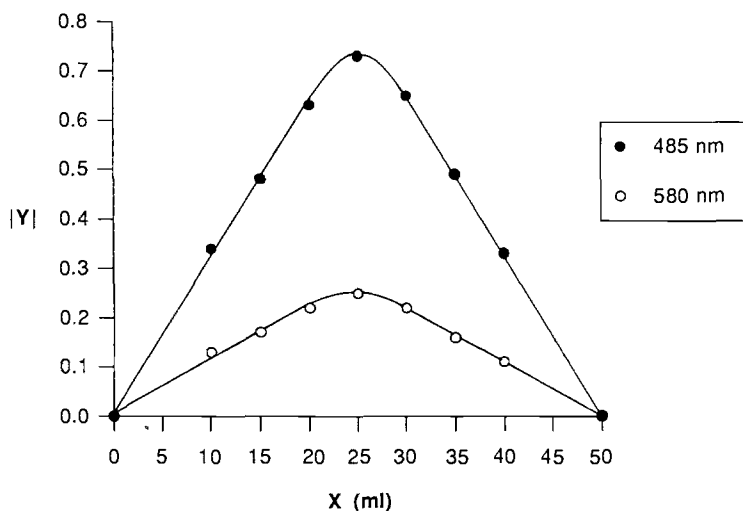


FIG. 4—Results of the Job's method analysis of the complex formed between RP and ZnI_2 (parameters as defined in Table 1).

The results indicated that the complex formed in solution between RP and ZnI_2 had a RP-metal ratio of 1 : 1. As the same result was obtained at different wavelengths, it appeared that a single complex was being formed [12]. From the absorbance values recorded, the molar extinction coefficient for the RP-Zn complex was calculated to be 57 400 (± 1000) at 485 nm.

Cadmium (II) Complex

Evaluation of the complex formed between RP and cadmium iodide (CdI_2) was approached in the same manner as for the RP-Zn complex. The absorbance values observed are shown in Table 2 and the resulting plot of |Y| against X in Fig. 5. As for the RP-Zn

TABLE 2—Absorbance data and calculated values for the Job's method analysis of the complex formed between RP and CdI_2 .

X, ^a mL	Abs. at 505 nm			Abs. at 580 nm		
	Obs.	Calc. ^b	Y ^c	Obs.	Calc. ^b	Y ^c
0	0.161	0.161	0.000	0.575	0.575	0.000
10	0.327	0.129	0.198	0.326	0.460	0.134
15	0.406	0.113	0.293	0.237	0.402	0.165
20	0.464	0.097	0.367	0.133	0.345	0.212
25	0.470	0.081	0.389	0.067	0.287	0.220
30	0.424	0.064	0.360	0.032	0.230	0.198
35	0.334	0.048	0.286	0.017	0.172	0.155
40	0.227	0.032	0.195	0.007	0.115	0.108
50	0.000	0.000	0.000	0.000	0.000	0.000

^aVolume (mL) of metal salt solution added to (50 - X) mL of RP solution.

^bCalculated absorbance assuming no reaction.

^cAbsolute value of the difference between observed and calculated values.

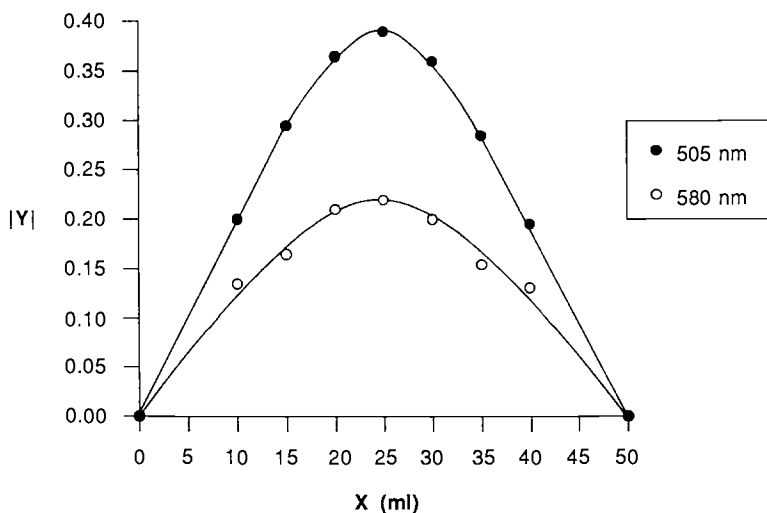


FIG. 5—Results of the Job's method analysis of the complex formed between RP and CdI_2 (parameters as defined in Table 2).

complex, the results indicated that the RP-metal ratio was 1 : 1 and that a single complex was being formed. The molar extinction coefficient for the RP-Cd complex was calculated to be 36 900 (± 800) at 505 nm.

Mercury (II) Complex

The complex formed between RP and mercuric chloride ($HgCl_2$) was evaluated in a manner analogous to the previous two complexes. The recorded absorbances are shown in Table 3 and the plot of $|Y|$ against X shown in Fig. 6. The results also suggested that a RP-metal ratio of 1 : 1 was likely and that only one compound was formed under the conditions of the experiment. However, the value of X for which $|Y|$ was a maximum was less well defined

TABLE 3—Absorbance data and calculated values for the Job's method analysis of the complex formed between RP and $HgCl_2$.

X, ^a mL	Abs. at 522 nm			Abs. at 580 nm		
	Obs.	Calc. ^b	Y ^c	Obs.	Calc. ^b	Y ^c
0	0.247	0.247	0.000	0.566	0.566	0.000
10	0.281	0.197	0.084	0.396	0.453	0.057
15	0.305	0.173	0.132	0.309	0.396	0.087
20	0.329	0.148	0.181	0.214	0.340	0.126
25	0.335	0.123	0.212	0.143	0.283	0.140
30	0.300	0.099	0.201	0.094	0.226	0.132
35	0.245	0.074	0.171	0.059	0.170	0.111
40	0.182	0.049	0.133	0.030	0.113	0.083
50	0.000	0.000	0.000	0.000	0.000	0.000

^aVolume (mL) of metal salt solution added to (50 - X) mL of RP solution.

^bCalculated absorbance assuming no reaction.

^cAbsolute value of the difference between observed and calculated values.

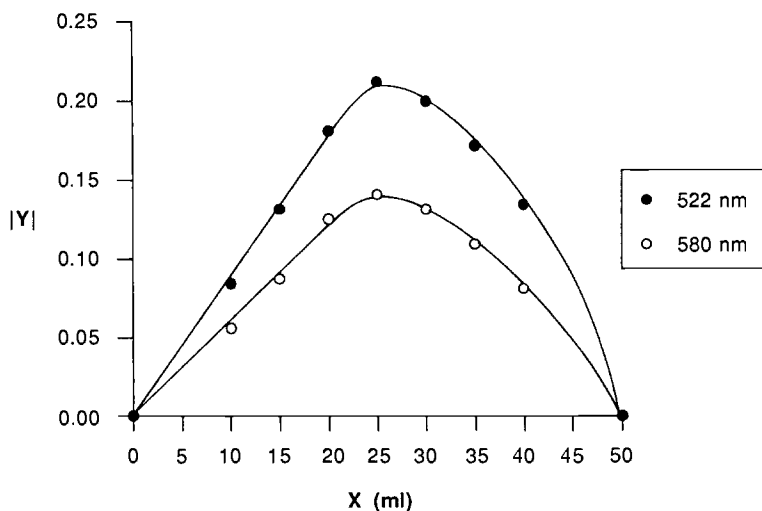


FIG. 6—Results of the Job's method analysis of the complex formed between RP and $HgCl_2$ (parameters as defined in Table 3).

than for the Zn(II) and Cd(II) complexes. The molar extinction coefficient, assuming a 1 : 1 RP-metal ratio, was calculated to be $27\,100 (\pm 600)$ at 522 nm.

The results for the RP-Hg complex were not in agreement with those obtained by previous workers [3, 4] who reported a RP-metal ratio of 2 : 1. Burkina and Senov [3], however, noted that the ratio was dependent on the relative concentrations of the two reagents. Stoilovic and co-workers [5] reported that the fluorescence spectrum of the RP-Hg complex varied considerably depending on the anion of the mercury salt and the amount of water present. It is therefore possible that a number of structures, with different RP-metal ratios, are possible for the RP-Hg complex depending on the conditions employed.

Crystal Structure of [Cd(RP)I(H₂O)₂].THF

Crude metal complexes of RP were prepared by treating RP with an excess of the corresponding metal salt [ZnI₂, Zn(NO₃)₂, ZnCl₂, CdI₂, Cd(NO₃)₂, and HgCl₂] in aqueous solution. In each case, the crude complex was obtained as a red powdery solid.

The complex from CdI₂ was dissolved in tetrahydrofuran (THF) and purified by Sephadex chromatography. Ether diffusion into a solution of the purified complex yielded red needles of [Cd(RP)I(H₂O)₂].THF (m.p. 333–4°C), the structure of which was determined by X-ray diffraction. Attempts to prepare crystals of the other complexes, suitable for X-ray studies, were unsuccessful (the zinc compounds, for example, have extremely low solubility).

The compound, C₂₂H₂₀CdINO₇, M = 649.5, crystallizes in the triclinic space group P $\bar{1}$, with $a = 8.243(2)$, $b = 10.679(3)$, $c = 13.551(2)$ Å; $\alpha = 84.03(2)$, $\beta = 86.86(1)$, $\gamma = 84.32(2)^\circ$; $V = 1179$ Å³, $D_c = 1.83$ and $D_m = 1.84(1)$ g cm⁻³; crystal size 0.05 by 0.12 by 0.35 mm; and μ (MoK α) = 22.4 cm⁻¹; with two formula units in the unit cell.

The crystals are rapidly destroyed by X-rays at room temperature and intensity data were therefore collected at 193K. The crystal eventually decomposed abruptly, curtailing the data collection slightly [2741 possible reflections, 2475 "observed" with $I > 3\sigma(I)$]. The structure was solved by conventional "heavy atom" techniques and has at present been refined to $R = 0.042$ ($R_w = 0.059$). Hydrogen atoms on the aromatic carbon atoms were located in a different Fourier synthesis and included as a fixed contribution in structure factor calculations. The THF molecule, which is present as a noncoordinated solvent of crystallization, shows considerable disorder as does one of the coordinated water molecules. It has therefore been impossible to locate the water and THF hydrogen atoms with any certainty.

The structure (Fig. 7) differs from that proposed by other workers [7,8] for the RP-metal complexes. Cadmium is six coordinate and each cadmium atom binds one molecule of RP, which acts as a tridentate ligand, with iodine and two water molecules completing a distorted octahedral coordination environment. There are no significant differences between bond distances in the two 1,3-indandione moieties of the ligand. The two N—C bonds are 1.322(9) and 1.318(9) Å and the C—N—C bond angle is 133.0(6)°. The two virtually planar 1,3-indandione systems are not coplanar, presumably because of steric repulsion between the two noncoordinated carbonyl oxygens O3A and O3B. The angle between the two planes is 19.5° and the O3A—O3B distance is 2.68 Å.

The crystal structure of the RP-Cd complex is reminiscent of the purpurate complexes reported by White and co-workers [13–20]. The purpurate anion coordinates to metals in a manner analogous to RP and the stoichiometry of the resulting complexes in solution are almost exclusively 1:1 metal-ligand derivatives.

The crystal structure of protonated Ruhemann's purple (RPH) has been reported by Grigg and co-workers [21]. As was found for the cadmium complex, there is no significant difference between the two halves of the RPH molecule [for example, N—C bonds are 1.340(5) and 1.346(4) Å]. The C—N—C bond angle is 127.9(3)° and repulsion between the adjacent oxygen atoms is relieved by rotation of each 1,3-indandione moiety by about 20° around the C—N bonds. The crystal structure of the ligand in the Cd-RP complex is therefore consistent with the reported crystal structure of RPH [21].

RP-Metal Complexes in Fingerprint Enhancement

The fluorescence spectrum of [Cd(RP)I(H₂O)₂] (3; M = Cd, X = I) in ethanol, recorded at 77K, was found to be identical with that observed at the same temperature for a ninhydrin-developed fingerprint after Cd(II) treatment [5]. This indicated that a complex of the type isolated was responsible for the luminescent behavior of the treated fingerprints. Spectra of Zn(II)- and Hg(II)-treated prints, together with the results from the Job's method

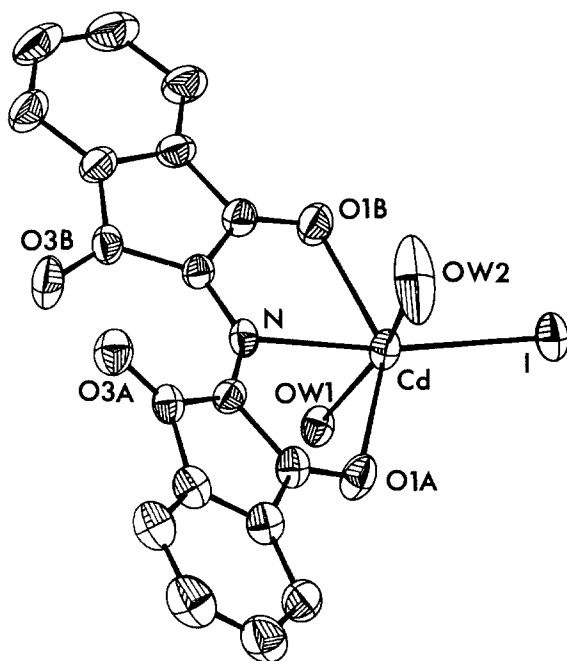


FIG. 7—ORTEP diagram of $[Cd(RP)I(H_2O)_2]$. (Hydrogen atoms are now shown.) Atoms are shown as 50% probability ellipsoids. Bond lengths (\AA) and angles ($^\circ$) around cadmium: Cd-I, 2.721(1); Cd-O1A, 2.390(5); Cd-O1B, 2.387(5); Cd-N, 2.386(6); Cd-OW1, 2.348(5); Cd-OW2, 2.315(6); I-Cd-O1A, 113.7(1); I-Cd-O1B, 104.0(1); I-Cd-N, 170.5(1); I-Cd-OW1, 102.0(1); I-Cd-OW2, 93.9(2); N-Cd-O1A, 71.4(2); N-Cd-O1B, 71.5(2); O1A-Cd-O1B, 142.3(2); OW1-Cd-OW2, 163.9(2); N-Cd-OW1, 86.0(2); N-Cd-OW2, 78.3(3); O1A-Cd-OW1, 86.0(2); O1A-Cd-OW2, 85.6(2); O1B-Cd-OW1, 84.6(2); O1B-Cd-OW2, 93.7(3). (The remaining bond distances and angles and atomic coordinates for this structure are available from the authors on request.)

analysis, suggested that compounds of similar structure (3) (Fig. 2) are responsible for the observed luminescence.

The nature of the counter-ion in the zinc and cadmium complexes does not affect the spectra markedly and the selection of a metal salt for secondary treatment of fingerprints developed with ninhydrin is made on the basis of desirable solubility properties [5]. On the other hand, water has been found to be a necessary component in the complexation process and this explains why the presence of moisture is required when enhancing fingerprints [5].

Acknowledgments

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