

Philip J. Davies,<sup>1</sup> B.Sc.; Hilton J. Kobus,<sup>2</sup> Ph.D.; Max R. Taylor,<sup>1</sup> Ph.D.; and Kevin P. Wainwright,<sup>1</sup> Ph.D.

## Synthesis and Structure of the Zinc(II) and Cadmium(II) Complexes Produced in the Photoluminescent Enhancement of Ninhydrin Developed Fingerprints Using Group 12 Metal Salts

**REFERENCE:** Davies, P. J., Kobus, H. J., Taylor, M. R., and Wainwright, K. P., "Synthesis and Structure of the Zinc(II) and Cadmium(II) Complexes Produced in the Photoluminescent Enhancement of Ninhydrin Developed Fingerprints Using Group 12 Metal Salts," *Journal of Forensic Sciences*, JFSCA, Vol. 40, No. 4, July 1995, pp 565-569.

**ABSTRACT:** The complexation reactions involving Ruhemann's purple (RP) and either zinc(II) or cadmium(II), which are made use of in the enhancement of latent fingerprints that have undergone preliminary development with ninhydrin, have been investigated under a variety of conditions. Contrary to earlier reports it is now clear that metal complexes with either a 1:1 or 1:2 metal:ligand ratio can be formed under certain conditions. Polar solvents, which cause extensive ionization of the metal salt, facilitate the formation of the 1:2 complex whereas less polar solvents allow the formation of 1:1 complexes through retention of a covalently bound anion in the primary coordination sphere. Thus,  $Zn(RP)_2$  can be prepared from seemingly any zinc(II) salt and NaRP in water or methanol. It is a highly insoluble and kinetically stable red powder with fluorescence emission bands at 590 and 640 nm. The structure of an orange 1:1 Zn:RP complex, produced as crystals from  $ZnCl_2$  and NaRP in a 5:1 chloroform:methanol mixture, has been solved by X-ray diffraction and shown to correspond to a formula of  $NaZn_2(RP)_2Cl_3 \cdot CH_3OH$ . This material is very rapidly decomposed into its components by water. The previously reported 1:1 Cd:RP complexes, which are red, form under a much wider range of conditions than their zinc(II) counterparts, however, if cadmium(II) perchlorate is combined with RP in water or methanol Cd(RP)<sub>2</sub> precipitates instead. This is a golden-brown powder showing a strong fluorescence.

**KEYWORDS:** criminalistics, fingerprints, ninhydrin, Ruhemann's purple, zinc, cadmium, photoluminescence, X-ray diffraction

The reaction between ninhydrin (2,2-dihydroxy-1,3-indanedione) and amino acids secreted from the eccrine glands to form the product known as Ruhemann's purple (RP) is the basis for detection of fingerprints on absorbent surfaces such as paper. If ninhydrin developed fingerprints are treated with zinc(II) chloride solution, an orange colored complex that has strong photoluminescent properties is formed, resulting in a significant improvement in detection

Received for publication 19 Aug. 1994; revised manuscript received 24 Oct. 1994; accepted for publication 8 Nov. 1994.

<sup>1</sup>Research Student and Senior Lecturers, respectively, School of Physical Sciences, The Flinders University of South Australia, Adelaide, South Australia.

<sup>2</sup>Chief Scientist, Forensic Science Centre, Adelaide, South Australia.

sensitivity [1]. The intensity of the photoluminescence is increased by cooling the fingerprints in liquid nitrogen [2]. It has also been noted that some moisture is necessary to promote formation of the complex (> 50% relative humidity). Atmospheric humidity is usually sufficient, but in very dry conditions light steaming of the complex may be necessary.

Kobus et al. [2] provided evidence for the formation of a second zinc(II) complex when ninhydrin developed fingerprints were processed with zinc(II) chloride. A red colored complex appeared to be formed in the presence of a high level of RP (strong ninhydrin fingerprints) and excess moisture (> 80% relative humidity). The orange complex was characterized by a photoluminescent emission band at 540 nm (excitation 490 nm) while the red complex resulted in the emergence of a band at 590 nm. Since the main application of the zinc(II) complexation procedure was for the enhancement of weak ninhydrin fingerprints (low RP levels) the red complex appeared unlikely to influence practical fingerprint work.

Stoilovic et al. [3] showed that the orange zinc(II) complex was unstable in the presence of excess moisture. The addition of water to an ethanolic solution resulted in dissociation to RP. This instability resulted in inconsistent results on highly absorbent papers such as newsprint. They investigated the complexing properties of the other Group 12 metals (formerly known as Group IIb metals) and showed that cadmium(II) formed a red colored complex with strong photoluminescence at low temperature (excitation maximum 510 nm, emission maximum 585 nm). It was stable in the presence of moisture and the red shifted emission maximum overcame background problems on surfaces such as yellow postal envelopes. Cadmium(II) complexation, therefore, offered advantages over zinc(II) for fingerprint enhancement.

These observations, although suggesting the existence of two zinc(II) complexes, are largely empirical. Lennard et al. [4] isolated a cadmium(II)-RP complex and determined its crystal structure by X-ray diffraction. The complex showed a 1:1 metal:ligand ratio and, on the basis of spectroscopic data, they proposed that complexation of RP with zinc(II) occurs in the same way. Previously it had been believed that the Group 12 metal complexes of RP had a 1:2 metal:ligand ratio [5,6].

The purpose of the work reported in this paper was to explain the observed zinc(II) chemistry by exploring the possibility that RP complexes with a metal:ligand ratio other than 1:1 may form under certain conditions; it being felt that a better understanding

of the complexation chemistry would then allow improved and more reproducible fingerprint enhancement procedures to be developed.

## Materials and Methods

### Ligand Synthesis

The sodium salt of Ruhemann's purple was prepared using the method of Moore and Stein, [7] which involved reacting glycine with ninhydrin in sodium citrate buffer (pH 5.1).

### Complex Synthesis in Solution

The complexes were prepared by combining a solution of the metal salt with a suspension of NaRP in methanol (although NaRP has some solubility in methanol it was not fully dissolved in the amounts of solvent used in the preparations described below). These conditions represent an approximation to the conditions that are encountered in actual fingerprint enhancement work where RP is dealt with in the solid state. The effect of the variations in the reaction stoichiometry, the polarity of the reaction medium (solvent), and the anion species were investigated.

**Stoichiometry**—The stoichiometry was varied to provide either a 1:1 or a 1:2 metal:ligand ratio.

**Solvent**—Water and methanol were used to simulate reactions in a polar medium. A 5:1 chloroform:methanol mixture was used to represent less polar conditions on or within an absorbent material. The methanol was necessary to aid dissolution of the metal salt.

**Anion Species**—Weakly coordinating perchlorate and the more strongly coordinating chloride ion were used. The strongly complexing thiocyanate ion was also utilized to check for the possible inclusion of anions in a complex. Its presence is easily detectable by virtue of the very strong absorbance in the infrared spectrum at 2 porcyimatein  $2\ 100\ \text{cm}^{-1}$  arising from the stretching of the carbon to nitrogen triple bond. The fact that infrared spectroscopy can easily be carried out in the solid state made this a very useful technique to apply to the highly insoluble materials encountered in this work, which could not always be characterized using solution techniques.

**Cation Species**—It is recognized that when RP is formed in situ, through reaction of the amino acids in a fingerprint with ninhydrin sprayed onto the surface supporting the fingerprint, the cation may well be one other than sodium, however, this point was not investigated. Sodium was the cation of choice because of its high abundance in both paper and the secretions from eccrine glands [8]. Complexation with protonated RP was not studied as it seems likely that there is little of this formed when the enhancement is carried out at the usual pH of 4.5 to 5.2. Spectrophotometric studies have shown that the purple color of RP is fully developed in solutions whose pH is increased into the upper part of this range [9].

**Complex Preparation**—The previously unreported complexes that were isolated during the course of this investigation, and which have been fully characterized, are best prepared using the procedures that follow. Hydrated metal(II) perchlorates used in the syntheses were obtained by neutralizing an aqueous suspension of the appropriate carbonate (obtained commercially: cadmium(II) carbonate from B.D.H., basic zinc(II) carbonate ( $\text{ZnCO}_3 \cdot 2\text{ZnO} \cdot$

$3\text{H}_2\text{O}$ ) from May and Baker) with concentrated perchloric acid. The resulting solution was filtered and then evaporated until precipitation of the perchlorate salt occurred. This was collected by filtration and dried under vacuum. Anhydrous zinc chloride was obtained from Merck, cadmium chloride hemipentahydrate from Ajax (Australia) and anhydrous zinc thiocyanate from B.D.H.

**Zn(RP)<sub>2</sub>**—A solution of zinc(II) perchlorate hexahydrate (57.3 mg, 0.154 mmol), dissolved in anhydrous methanol (10 mL) was added dropwise to a stirred refluxing suspension of NaRP (100.2 mg, 0.308 mmol) in anhydrous methanol (50 mL) over a 10 min period. The suspension was refluxed for a further 3 h during which time the suspended material changed color from deep purple to bright red. After cooling the mixture the suspended product was collected by filtration, washed thoroughly with hot methanol ( $2 \times 10\ \text{mL}$ ) and dried *in vacuo* (93 mg, 90%), m.p.  $> 300^\circ\text{C}$ , (Found: C, 64.2; H, 2.4; N, 4.3; Zn, 9.8.  $\text{C}_{36}\text{H}_{16}\text{N}_2\text{O}_8\text{Zn}$  requires C, 64.5; H, 2.4; N, 4.2; Zn, 9.8%). Infrared spectrum: (thin layer formed from evaporation of a  $\text{CCl}_4$  mull)  $1722\ \text{cm}^{-1}$  (w),  $1702$  (w),  $1640$  (s),  $1599$  (m),  $1502$  (s),  $1450$  (m),  $1319$  (s),  $1292$  (s),  $1199$  (s),  $1142$  (s),  $1122$  (s),  $1082$  (m),  $1060$  (s),  $1002$  (s),  $915$  (m),  $738$  (m),  $599$  (m). Visible spectrum:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ )  $494\ \text{nm}$  ( $\epsilon/\text{M}^{-1}\ \text{cm}^{-1}$  110 000).

**NaZn<sub>2</sub>(RP)<sub>2</sub>Cl<sub>3</sub>CH<sub>3</sub>OH**—Under an atmosphere of dry argon a solution of anhydrous zinc(II) chloride (42 mg, 0.31 mmol) dissolved in anhydrous methanol (10 mL) was slowly added over a 10 min period to a stirred refluxing suspension of NaRP (100 mg, 0.31 mmol) in chloroform (50 mL). The mixture was heated at reflux for 6 h during which time a clear orange solution resulted. Diethyl ether vapor diffusion into the orange solution over a period of 7 to 14 days gave the product as orange crystals (42 mg, 30%), m.p.  $300^\circ\text{C}$  with decomposition, (Found: C, 50.2; H, 2.5; N, 2.8; Cl, 13.1; Zn, 14.6%.  $\text{C}_{37}\text{H}_{20}\text{Cl}_3\text{N}_2\text{NaO}_9\text{Zn}_2$  requires C, 49.6; H, 2.3; N, 3.1; Cl, 11.9; Zn, 14.6%). Infrared spectrum: (thin layer formed from evaporation of a  $\text{CCl}_4$  mull)  $1722\ \text{cm}^{-1}$  (w),  $1702$  (w),  $1650$  (s),  $1585$  (m),  $1500$  (s),  $1422$  (s),  $1322$  (s),  $1210$  (s),  $1155$  (m),  $1060$  (m),  $1000$  (w),  $980$  (w),  $910$  (w),  $802$  (w),  $779$  (w),  $738$  (s),  $598$  (s). Visible spectrum:  $\lambda_{\text{max}}$  (EtOH)  $486\ \text{nm}$  ( $\epsilon/\text{M}^{-1}\ \text{cm}^{-1}$  57 000).

**Cd(RP)<sub>2</sub>**—This complex was produced by a procedure analogous to that used for Zn(RP)<sub>2</sub>. The product formed as a golden-brown powder in 90% yield, m.p.  $> 300^\circ\text{C}$ , (Found: C, 60.0; H, 2.3; Cd, 15.1; N, 3.9.  $\text{C}_{36}\text{H}_{16}\text{CdN}_2\text{O}_8$  requires C, 60.3; H, 2.2; Cd, 15.8; N, 3.9%). Infrared spectrum: (thin layer formed from evaporation of a  $\text{CCl}_4$  mull)  $1718\ \text{cm}^{-1}$  (w),  $1700$  (m),  $1618$  (m),  $1599$  (m),  $1498$  (s),  $1440$  (m),  $1355$  (w),  $1320$  (s),  $1288$  (s),  $1200$  (s),  $1145$  (m),  $1110$  (m),  $1082$  (m),  $1055$  (s),  $1002$  (s),  $908$  (w),  $802$  (m),  $780$  (w),  $738$  (m),  $708$  (w),  $700$  (w),  $650$  (w),  $598$  (m). Visible spectrum:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ );  $504\ \text{nm}$  ( $\epsilon/\text{M}^{-1}\ \text{cm}^{-1}$  70 000).

**CdCl(RP)CH<sub>3</sub>OH**—A solution of cadmium(II) chloride hemipentahydrate (35.2 mg, 0.154 mmol) in anhydrous methanol (10 mL) was added over a ten minute period to a stirred refluxing suspension of NaRP (50.1 mg, 0.154 mmol) in anhydrous methanol (50 mL). The mixture was heated under reflux for three hours during which time the purple suspension became deep red. The product was collected by filtration washed thoroughly with hot methanol ( $2 \times 10\ \text{mL}$ ) and dried *in vacuo* (67 mg, 90%), m.p.  $> 300^\circ\text{C}$ , (Found: C, 47.3; H, 2.4; N, 2.9.  $\text{C}_{19}\text{H}_{12}\text{CdClNO}_5$  requires C, 47.3; H, 2.5; N, 2.9%). Infrared spectrum: (thin layer formed

from evaporation of a  $\text{CCl}_4$  mull) 1718  $\text{cm}^{-1}$  (w), 1690 (m), 1655 (s), 1635 (s), 1590 (s), 1490 (s), 1450 (s), 1350 (m), 1318 (s), 1210 (s), 1150 (m), 1125 (m), 1085 (m), 1065 (s), 1002 (m), 955 (w), 910 (w), 800 (w), 780 (m), 735 (m), 655 (m), 598 (m). Visible spectrum:  $\lambda_{\text{max}}$  (EtOH): 505 nm ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$  37 000).

### Complex Synthesis on Paper

An aqueous solution of RP was prepared by mixing a 1% solution of glycine with a 1% solution of ninhydrin. Serial dilutions were made to provide a range of RP concentrations from 1% to 0.05%. A single drop of each solution was spotted onto a filter paper and dried to provide a range of RP intensities on paper. The zinc(II) complexes were developed by spotting a drop of a 1% zinc(II) chloride solution onto the RP spots. The solvent was either methanol to provide a polar medium or a 1:12 methanol:freon mixture as a less polar medium.

### Analysis of the Complexes

**Composition**—Microanalyses carried out by the Australian Microanalytical Service, Notting Hill, Victoria, was the primary method used to provide metal to ligand ratio information. This was supported by infrared absorption measurements carried out using a Perkin-Elmer 297 Infrared Spectrophotometer.

**Photoluminescence**—Visual observation was made using a filtered xenon arc lamp as an excitation source (Polilight, Rofin Australia). Emission and excitation spectra of solid complexes were measured using a Perkin-Elmer fluorescence spectrometer with cryogenic attachment. Emission spectra of the complexes developed on paper were measured using a Colorite Microspectrophotometer (Rofin Australia) with a Polilight as excitation source.

## Results and Discussion

### The Complexes Formed in Solution

The products formed by the reaction between zinc(II) or cadmium(II) and NaRP in methanol are shown in Table 1. It is evident from this that irrespective of the ratio of metal to ligand employed, or the anion present, zinc(II) always precipitates from methanol as  $\text{Zn}(\text{RP})_2$ , which is bright red, even when a 1:1 reaction stoichiometry exists. Similarly for cadmium(II); only  $\text{Cd}(\text{RP})_2$  forms when the anion is the weakly coordinating perchlorate ion, however, when more strongly binding chloride is the anion the stoichiometry of the reaction determines the product. This is somewhat surprising since it is well established that the thermodynamic bind-

ing constant for the incorporation of a second ligand into the primary coordination sphere of a metal ion is lower than the binding constant for the first (unless special circumstances, not in existence here, prevail). That is,  $K_1$  (Equation 1, where  $M$  = metal,  $X$  = anion) is expected to



be  $> K_2$  (Equation 2). Accordingly, when a 1:1 ratio of metal:ligand is present the 1:1 complex would be expected to be dominant at equilibrium in solution, with only relatively small amounts of the 1:2 complex and free  $\text{M}^{2+}$  present. It is clear therefore, from the exclusive precipitation of neutral  $\text{Zn}(\text{RP})_2$ , in a situation where there is insufficient RP for complete conversion of all  $\text{Zn}^{2+}$  to this species, that the equilibrium is being driven to the right hand side of Equation 2 because of the low solubility of the  $\text{M}(\text{RP})_2$  species compared to  $\text{M}(\text{RP})\text{X}$  ( $X$  = the resident anion), which causes the former to precipitate but not the latter. Evidence for this also comes from the fact that after precipitation is complete and the  $\text{Zn}(\text{RP})_2$  has been filtered off, the filtrate is not red, but rather displays the characteristic orange color of  $\text{Zn}(\text{RP})\text{X}$  species. Displacement of the equilibrium is only possible if the unprecipitated  $\text{M}(\text{RP})\text{X}$  can disproportionate, as shown in Equation 3. This is a process that will become favored as the dielectric constant for the



reaction medium increases. The tendency for the formation of  $\text{M}(\text{RP})_2$  will reduce if a situation prevails where the insolubility of  $\text{M}(\text{RP})\text{X}$  and  $\text{M}(\text{RP})_2$  is comparable. This appears to be the case for  $M = \text{Cd}^{2+}$  and  $X = \text{Cl}^-$  in methanol; where the precipitated product is  $\text{Cd}(\text{RP})\text{ClCH}_3\text{OH}$  when the ratio of  $\text{CdCl}_2$ :RP used is 1:1. In water, where the solubility of  $\text{Cd}(\text{RP})\text{Cl}$  is higher and its tendency to dissociate greater, because of the higher dielectric constant of the medium, only  $\text{Cd}(\text{RP})_2$  formed, irrespective of the reaction stoichiometry.

To isolate an orange colored  $\text{Zn}(\text{RP})\text{X}$  species so that its solid state structure and properties could be investigated it became apparent from the observations noted above that it would have to be formed with a tightly binding anion and in conditions of low dielectric constant. We were successful in achieving this through the reaction of  $\text{ZnCl}_2$  with NaRP, in a 1:1 ratio, in a 5:1 chloroform:methanol mixture, followed by precipitation of the product through the diffusion of diethyl ether vapor into the reaction mixture. Microanalysis of the orange crystalline precipitate indicated that it had the formula  $\text{NaZn}_2(\text{RP})_2\text{Cl}_3\text{CH}_3\text{OH}$  and subsequent X-ray analysis [10] showed that the structure, shown in Fig. 1, involves two five coordinate zinc(II) ions each bound by one tridentate RP, but with one zinc(II) ion binding, in addition, two chloride ions, whereas the other binds one chloride ion and one coordinated molecule of methanol. The two half-units are linked by a sodium ion coordinating intramolecularly to the two exposed keto groups of each half-unit and intermolecularly to two chlorides.

### The Complexes Formed on Paper

When the zinc(II) complexes were formed on paper the governing factor was the concentration of the RP. The more strongly

TABLE 1—Products derived from the reaction of either a zinc(II) salt or a cadmium(II) salt with NaRP in methanol as changes in the anion or the reaction stoichiometry are made.

Anion	Reaction Stoichiometry ( $\text{M}^{2+}$ :NaRP)	Zinc(II) Product	Cadmium(II) Product
$\text{ClO}_4^-$	1:2	$\text{Zn}(\text{RP})_2$	$\text{Cd}(\text{RP})_2$
	1:1	$\text{Zn}(\text{RP})_2$	$\text{Cd}(\text{RP})_2$
$\text{Cl}^-$	1:2	$\text{Zn}(\text{RP})_2$	$\text{Cd}(\text{RP})_2$
	1:1	$\text{Zn}(\text{RP})_2$	$\text{Cd}(\text{RP})\text{ClCH}_3\text{OH}$
$\text{SCN}^-$	1:2	$\text{Zn}(\text{RP})_2$	<sup>a</sup>
	1:1	$\text{Zn}(\text{RP})_2$	<sup>a</sup>

<sup>a</sup>Reaction not carried out.

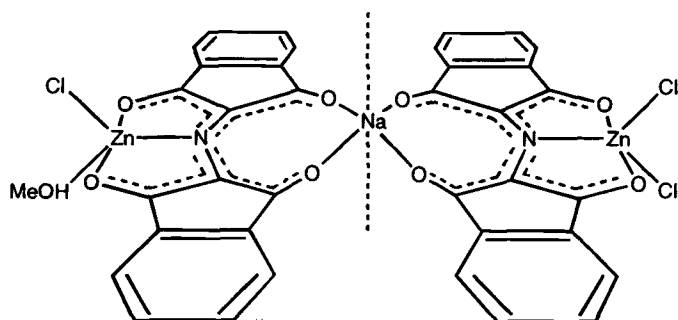


FIG. 1—Structure of  $\text{NaZn}_2(\text{RP})_2\text{Cl}_3\text{CH}_3\text{OH}$ ; the orange complex isolated by Davies [10] from the reaction of zinc(II) chloride with the sodium salt of Ruhemann's purple in a 1:1 molar ratio in a solvent of low polarity (5:1 chloroform:methanol).

colored RP spots on paper became deep red on treatment with  $\text{ZnCl}_2$ , indicating the presence, predominantly, of  $\text{Zn}(\text{RP})_2$ . As the RP concentration was decreased treatment with  $\text{ZnCl}_2$  produced progressively more intensely colored orange spots, indicative of a  $\text{Zn}(\text{RP})\text{Cl}$  species, until in the most weakly colored RP spots the orange color dominated. The same results were obtained for both methanol and freon as the solvent for the  $\text{ZnCl}_2$ . Similar results were obtained for strong and weak fingerprints deposits. These results are broadly in accordance with those obtained in solution, but indicate that on paper, where ion diffusion is more limited, the disproportionation process giving  $\text{Zn}(\text{RP})_2$  is disfavored.

#### Stability of the Complexes in Aqueous Conditions

Water was added to dilute solutions of the 1:1 zinc(II) and cadmium(II) complexes ( $2.5 \times 10^{-5}$  M in methanol) and any color change in the solution monitored spectrophotometrically. For the zinc(II) complex significant dissociation to RP had occurred within 30 s when the water content was increased to 10%. When the water content of the solution was 30%, only RP was observed after 30 s. For the cadmium(II) complex, on the other hand, minimal dissociation was observed after 30 s in 10% water and even in 50% water some complex was still present after this time. These results confirm the previous observations made regarding the instability of the orange zinc(II) complex in water [2,3]. The 1:2 complexes for both zinc(II) and cadmium(II) are so insoluble in water that they remain unchanged even when suspended in pure water.

#### Photoluminescence

Under Polilight illumination (450 to 520 nm) the solid  $\text{Zn}(\text{RP})_2$  and  $\text{Cd}(\text{RP})_2$  complexes produced strong photoluminescence emission at room temperature. The emission of the cadmium(II) complex was red shifted in comparison to the zinc(II) complex. Steaming and cooling in liquid nitrogen had no effect on their fluorescence. The solid  $\text{Cd}(\text{RP})\text{ClCH}_3\text{OH}$ , however, behaved quite differently. It showed no fluorescence until it was exposed to steam and cooled in liquid nitrogen. This observation is in accordance with the findings of Lennard [4] who solved the crystal structure of a fluorescent 1:1 Cd:RP complex (Fig. 2) and found that in addition to coordinated RP and iodide there are two water molecules coordinated in a *trans*-arrangement with respect to each other. Presumably the steaming process results in substitution of a single coordinated methanol by two coordinated water molecules.  $\text{NaZn}_2$ -

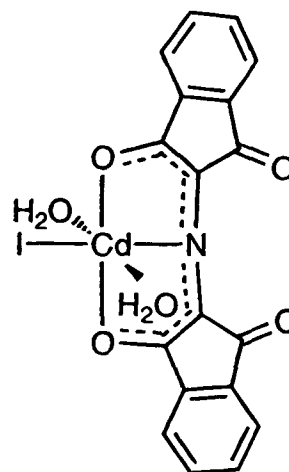


FIG. 2—Structure of  $\text{Cd}(\text{RP})(\text{H}_2\text{O})_2\text{I}$ ; the deep-red complex isolated by Lennard [4] from the reaction of cadmium(II) iodide with the sodium salt of Ruhemann's purple in a 1:1 molar ratio in water.

$(\text{RP})_2\text{Cl}_3\text{CH}_3\text{OH}$  also showed no significant fluorescence and in this case steaming or cooling with liquid nitrogen made no difference, indicating that this complex is not identical to the fluorescent complex that forms when the process is carried out on paper. This is not altogether surprising since the source of RP used in the formation of  $\text{NaZn}_2(\text{RP})_2\text{Cl}_3\text{CH}_3\text{OH}$  was NaRP, whereas on paper the cation associated with the RP probably varies with the type of paper and is not necessarily sodium(I). These observations highlight the sensitivity of fluorescence to minor changes in molecular structure and indicate the difficulties to be expected in obtaining reproducible results from different surfaces.

Photoluminescence intensity is related to molecular structure and Menzel et al. [11] have recognized that in RP complexes the most efficient photoluminescence occurs when the indanedione moieties are coplanar. For this to occur the two halves of the molecule must be held in place. This is achieved to some extent when a metal ion binds it as a tridentate ligand as shown in Figs. 1 and 2. In this arrangement energy loss by fluorescence is believed to be favored over intersystem crossing or internal conversion, processes that dominate in a nonplanar molecule. From the crystal structure of fluorescent  $\text{Cd}(\text{RP})(\text{H}_2\text{O})_2$  [4] it was shown that the tilt angle between the two indanedione moieties in the molecule is  $19.5^\circ$ . The crystal structure of the non-fluorescent  $\text{NaZn}_2(\text{RP})_2\text{Cl}_3\text{CH}_3\text{OH}$  [10], however, shows that its tilt angle is only approximately  $6.5^\circ$ , suggesting that factors, other than the tilt angle, play a role in determining the fluorescence properties of these molecules.

An interesting result emerged while studying the the fluorescence spectra of the red  $\text{Zn}(\text{RP})_2$  complex. The spectra shown in Fig. 3 are emission spectra obtained using excitation at around 500 nm with the sample cooled in liquid nitrogen. The spectrum obtained for the synthesized  $\text{Zn}(\text{RP})_2$  solid and for the red colored complex prepared on filter paper as outlined above, showed two peaks, one with a maximum at 590 nm and a larger peak with a maximum at 640 nm. A similar product formed from a very strongly developed ninhydrin fingerprint (made by repeatedly overlaying sweaty fingerprints) showed only the lower energy peak at 590 nm. This latter result is in agreement with results of Kobus et al. [2] obtained when the existence of the red zinc(II) complex was first noted. The reason for the difference is not apparent, but it appears that the zinc(II) 1:2 complex formed from reactions

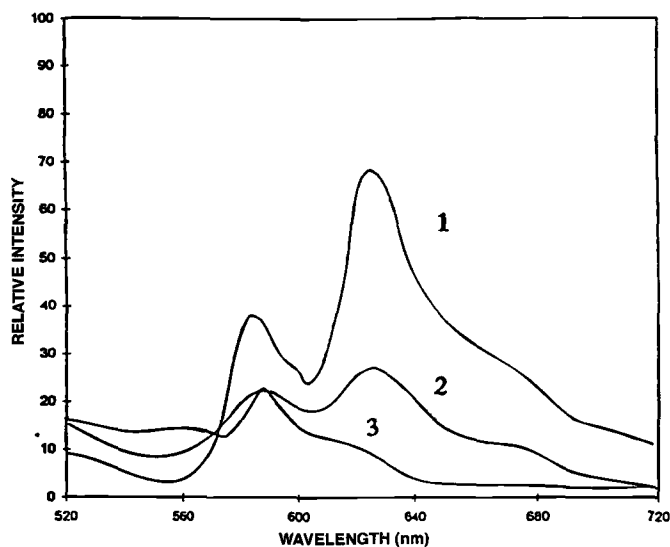


FIG. 3—Fluorescence emission spectra at 77 K, in response to excitation at 500 nm, arising from: (1) authentic  $Zn(RP)_2$  before, (2) a red spot produced on filter paper from the combination of glycine, ninhydrin and zinc(II) chloride (in that order), (3) a very strong fingerprint treated with ninhydrin followed by zinc(II) chloride, which caused it to develop a red coloration.

involving natural sweat is different to that formed from an amino acid.

### Conclusions

The work has shown that zinc(II) and cadmium(II) will form complexes with RP in both a 1:1 and 1:2 metal:ligand ratio depending on the reaction conditions. On paper surfaces, where ion diffusion is limited, the product appears to depend only on the concentration of the RP. Since in fingerprint work the purpose of the metal salt treatment is to enhance weak fingerprints, the level of RP will usually be very low and therefore the 1:1 complex will be dominant. However, there are occasions where it can be of use to treat strong fingerprints with metal salts to overcome colored or patterned backgrounds and in such instances the 1:2 complex may be encountered. For zinc(II) treatment it may therefore be useful to check for photoluminescent emission at both 590 and 540 nm.

The work has also confirmed the instability of the zinc(II) 1:1 complexes in water. When ninhydrin developed prints are treated with zinc(II) chloride steaming should be minimized or preferably avoided where atmospheric humidity is sufficient to allow the complex to develop unaided.

The more planar configuration of the zinc(II) 1:1 complex in comparison with the cadmium(II) analogue implies that zinc(II) salts should be preferred over cadmium(II) salts for fingerprint work. The instability of the zinc(II) 1:1 complexes does, however, affect their usefulness. Cadmium(II) on the other hand has toxicity problems. The solution is to have both treatments available, zinc(II) for use on normal good quality paper surfaces and cadmium(II) for

highly absorbent surfaces such as newsprint and where background problems are improved by the red shift of the cadmium(II) complex emission.

Although DFO (diazfluorenone) is making a significant impact as a photoluminescent reagent for processing fingerprints on paper [12], ninhydrin remains in wide use. The Group 12 metal salt treatment will therefore continue to be a valuable procedure for the enhancement of weak fingerprints. This and further improvements in the understanding of the chemistry of the process will assist in obtaining more consistent results.

### References

- [1] Herod, D. W. and Menzel, E. R., "Laser Detection of Latent Fingerprints: Ninhydrin Followed by Zinc Chloride," *Journal of Forensic Sciences*, Vol. 27, No. 3, July 1982, pp. 513-518.
- [2] Kobus, H. J., Stoilovic, M., and Warrenner, R. N., "A Simple Luminescent Post Ninhydrin Treatment for the Improved Visualisation of Fingerprints on Documents in Cases Where Ninhydrin Alone Gives Poor Results," *Forensic Science International*, Vol. 22, No. 2, July 1983, pp. 161-170.
- [3] Stoilovic, M., Kobus, H. J., Margot, P. A., and Warrenner, R. N., "Improved Enhancement of Ninhydrin Developed Fingerprints by Cadmium Complexation Using Low Temperature Photoluminescent Techniques," *Journal of Forensic Sciences*, Vol. 31, No. 2, April 1986, pp. 432-445.
- [4] Lennard, C. J., Margot, P. A., Sterns, M., and Warrenner, R. N., "Photoluminescent Enhancement of Ninhydrin Developed Fingerprints by Metal Complexation: Structural Studies of Complexes Formed Between Ruhemann's Purple and Group IIb Metal Salts," *Journal of Forensic Sciences*, Vol. 32, No. 3, May 1987, pp. 597-605.
- [5] Burkina, A. Y. and Senov, P. L., "Sodium Salt of Diketohydrindilydenediketohydrinamine as a Photometric Reagent for Lead, Mercury, and Bismuth Ions," *Zhurnal Analiticheskoi Khimii*, Vol. 27, No. 3, March 1972, pp. 473-478.
- [6] Kanke, M., Inoue, Y., Watanabe, H., and Nakamura, S., "Spectrophotometric Determination of Mercury by Using Ruhemann's Purple," *Bunseki Kagaku*, Vol. 21, pp. 622-626; from *Chemical Abstracts*, Vol. 77, 1972, abstr. 69702n.
- [7] Moore, S. and Stein, W. H., "Photometric Ninhydrin Method for Use in the Chromatography of Amino Acids," *Journal of Biological Chemistry*, Vol. 176, 1948, pp. 367-388.
- [8] Knowles, A. M., "Aspects of Physicochemical Methods for the Detection of Latent Fingerprints," *Journal of Physics. Section E*, Vol. 11, August 1978, pp. 713-721.
- [9] Lamothe, P. J. and McCormick, P. G., "Influence of Acidity on the Reaction of Ninhydrin with Amino Acids," *Analytical Chemistry*, Vol. 44, No. 4, April 1972, pp. 821-825.
- [10] Davies, P. J., Kobus, H. J., Taylor, M. R., and Wainwright, K. P., "Structure of the Reaction Product Obtained from the Interaction of the Sodium Salt of Ruhemann's Purple with Zinc(II) Chloride in a Solvent of Low Dielectric Strength," *Acta Crystallographica, Section C*, in press.
- [11] Menzel, E. R., Bartsch, R. A., and Hallman, J. L., "Fluorescent Metal-Ruhemann's Purple Coordination Compounds: Applications to Latent Fingerprint Detection," *Journal of Forensic Sciences*, Vol. 35, No. 1, Jan. 1990, pp. 25-34.
- [12] Pounds, C. A., Grigg, R., and Mongkolaussavaratana, T., "The Use of 1,8-Diazfluoren-9-one (DFO) for the Fluorescent Detection of Latent Fingerprints on Paper. A Preliminary Evaluation," *Journal of Forensic Sciences*, Vol. 35, No. 1, Jan. 1990, pp. 169-175.

Address requests for reprints or additional information to  
Kevin P. Wainwright, Ph.D.  
School of Physical Sciences  
Flinders University  
GPO Box 2100  
Adelaide, South Australia 5001