E. Roland Menzel,[1] Ph.D.; Richard A. Bartsch,[2] Ph.D.; and Johnny L. Hallman,[2] B.S.

Fluorescent Metal-Ruhemann's Purple Coordination Compounds: Applications to Latent Fingerprint Detection

ABSTRACT: Ruhemann's Purple (RP), the reaction product of ninhydrin with amino acids, forms coordination compounds with many metals. However, only a few of them fluoresce. A model for the structural and photophysical features that underlie the formation of fluorescent metal-RP compounds has been developed to establish guidelines for the design of optimized ninhydrin analogs and metal-RP complexes. The application of such complexes to the detection of latent fingerprints, a special surface analytical chemistry problem, is discussed.

KEYWORDS: criminalistics, fingerprints, ninhydrin, 5-methoxyninhydrin, Ruhemann's Purple, zinc chloride, twisted intramolecular charge transfer (TICT) compounds, fluorescence, lasers

In 1910, Ruhemann discovered the compound ninhydrin [1] and recognized that this compound reacts with amino acids, forming a purple-blue product, known as Ruhemann's Purple (*I*, Fig. 1) (RP). Ninhydrin soon became widely used as a universal reagent for amino acid assay in biochemical work.

In 1954, two Swedish biochemists, Oden and von Hofsten, reported another use of ninhydrin, namely its ability to develop latent fingerprints via reaction with amino acids of the palmar sweat residue which comprises latent prints [2]. Indeed, since the 1960s, ninhydrin has become the reagent par excellence for the development of latent prints on porous surfaces (mainly paper), an application one might classify as surface analytical chemistry.

Until 1976, latent fingerprints were developed by criminalists using procedures which relied on differences in absorption/reflectance of latent fingerprints and the surfaces on which they were found. In that year, a method for detecting latent prints by laser-excited *fluorescence* began to be developed to take advantage of the intrinsically high detection sensitivity fluorescence generally makes possible [3,4]. A particularly effective procedure consists of following the conventional ninhydrin treatment by reaction with zinc chloride. The reaction produces a coordination compound which is highly fluorescent under blue-
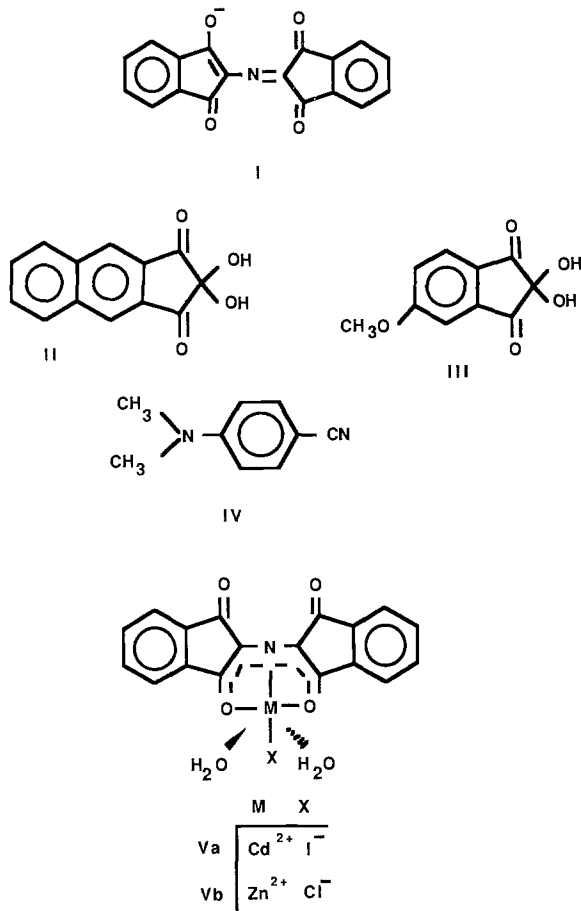
FIG. 1—*Structures of Ruhemann's Purple (I) benzo (f)ninhydrin (II), 5-methoxyninhydrin (III), dimethylaminobenzonitrile (IV), and metal-Ruhemann's Purple coordination compounds (Va, Vb).*

green excitation, typically from an argon-ion-laser. The details of this method are described elsewhere [5,6].

Since the early 1980s, ninhydrin analogs have been investigated as alternatives to ninhydrin, both in the conventional fingerprint detection mode [7] and for purposes of laser detection in concert with the zinc chloride ($ZnCl_2$) treatment. Benzo (*f*) ninhydrin (*II*, Fig. 1) was found to offer advantages over ninhydrin [8] when copper-vapor or frequency-doubled neodymium:yttrium aluminum garnet (Nd:YAG) lasers were used.

A particularly promising ninhydrin analog, 5-methoxyninhydrin (*III*, Fig. 1), was recently described by Almog and Hirshfeld [9]. This compound reacts well with amino acids. More importantly, the fluorescence obtained upon $ZnCl_2$ treatment is very much more intense than that achieved with ninhydrin/$ZnCl_2$. No other ninhydrin analogs that produce strongly fluorescent complexes have been found to date.

Latent prints developed with ninhydrin or its analogs can also be treated with cadmium salts to obtain fluorescent coordination compounds [10]. However, the fluorescence of the Cd-RP complex is substantially less intense than that of the zinc-RP complex [6,10]. Cadmium salt treatment is thus only used in instances in which background fluorescence from the surface holding a fingerprint is such that the orange Cd-RP fluorescence provides

better contrast than the yellow Zn-RP fluorescence when appropriate band-pass filters are used. No other effective (from the fluorescence standpoint) metal salt treatments have been found to date.

Several questions arise in connection with the Zn-RP complex, namely:

1. Why is RP, though intensely colored, nonfluorescent?
2. Why does the Zn-RP complexation cause a quite drastic color change (purple to yellow-orange) yielding a strongly fluorescent coordination compound?
3. What makes Zn^{2+} so unique in producing fluorescence?
4. What role does the seemingly innocuous 5-methoxy group play in the exceptionally intense fingerprint fluorescence obtained with the 5-methoxyninhydrin/$ZnCl_2$ treatment?

Answers to the above questions are of interest not only in the forensic science context, but also for the fluorescence assay of amino acids in general. Therefore, it is desirable to: (a) find new ninhydrin analogs with optimal chemical and spectroscopic properties and (b) select metals that will form coordination compounds which have desired spectroscopic features.

For the first point, the development of benzo(f)ninhydrin and 5-methoxyninhydrin are examples of what may be achieved, even if these reagents were developed without a firm concept of the structural and photophysical features that underlie the RP and Zn-RP spectroscopy. With the second point, the complex formed when RP reacts with europium chloride hexahydrate ($EuCl_3 \cdot 6H_2O$) displays intramolecular ligand to Eu energy transfer such that Eu luminescence results. This luminescence is long-lived. The complex is thus suited to time-resolved imaging for purposes of eliminating (short-lived) background fluorescence. This is discussed in a separate paper [11].

To explore the structural and photophysical features that cause the fluorescence of Zn-RP and similar complexes, coordination compound formation of RP with 21 metal salts has been examined. The spectroscopy of the complexes has been studied in solution (primarily in methanol, but also in water) as well as in solid samples (fingerprints).

Materials and Methods

The ninhydrin used to prepare RP and metal-RP complexes was obtained from Aldrich Chemical Company. The 5-methoxyninhydrin which was used in some experiments to prepare analogous complexes was synthesized by oxidation of 5-methoxy-1-indanone (Aldrich Chemical Company) with selenium dioxide in dioxane using the procedure of Almog and Hirshfeld [9]. The crude product was purified by column chromatography ($\times 2$) on silica gel with dichloromethane:ethyl acetate (3:1) as eluent, followed by radical chromatography on a silica gel plate with dichloromethane:ethyl acetate (5:1) as eluent and recrystallization from benzene-petroleum ether to give a deep yellow solid. The yellow solid changed at 99 to 103°C to reddish crystals, which melted sharply at 163°C to give a green liquid. Reported melting point (mp) 101 to 102°C [9]. ^1H NMR (200 MHz, $CD_3s(O)CD_3$) δ 3.98(s, 3H, OCH_3), 7.3 to 7.6 (m, 4H, aromatic + OH), 7.9 to 8.0 (m, 1H, aromatic).

Metal-RP Complexes in Solution

Ninhydrin was dissolved in methanol and the amino acid glycine was added, producing the characteristic blue-colored RP solution. For subsequent metal salt addition, concentrations of the RP solutions were adjusted to provide an optical density of about 1 (in 1-cm cuvettes). For assessment of solvent polarity effects, RP was also prepared in water in the same manner.

To form the metal complexes, metal salts were dissolved in methanol (or water). RP

solutions were then titrated with the salt solutions until completion of the solution color changes, which in most instances were pronounced and nearly instantaneous. Table 1 lists the metal ions studied. The salts were usually, but not always, metal chloride hydrates. At times, nitrates, acetates, iodides and perchlorates were also used. No significant effects of the anion species or the hydration of the salts were found. The metal salts were: $AlCl_3$; $CaCl_2 \cdot 2H_2O$; CdI_2; $Cd(NO_3)_2 \cdot 4H_2O$; $CeCl_3 \cdot 7H_2O$; $CrCl_3 \cdot 6H_2O$; $Cu(NO_3)_2 \cdot xH_2O$; $EuCl_3 \cdot 6H_2O$; $Eu(NO_3)_3 \cdot 6H_2O$; $HgCl_2$; KCl; $La(NO_3)_3 \cdot 6H_2O$; $MgCl_2 \cdot 6H_2O$; $MnCl_2 \cdot 4H_2O$; $Mn(ClO_4)_2 \cdot 6H_2O$; $NaCl$; $NdCl_3 \cdot 6H_2O$; $Ni(NO_3)_2 \cdot 6H_2O$; $RuCl_3 \cdot xH_2O$; $ScCl_3 \cdot xH_2O$; $SmCl_3 \cdot 6H_2O$; $SrCl_2 \cdot 6H_2O$; $TbCl_3 \cdot 6H_2O$; $ZnCl_2$; ZnI_2.

Metal-RP Complexes in Solid Form

The solid samples were fingerprints on white paper developed by spraying the paper with a methanol: 1,1,2-trichlorotrifluoroethane solution (1:4 by volume) of ninhydrin and incubating the paper at 40°C and 60% relative humidity for 1 h. The solution was prepared by first dissolving ninhydrin to near saturation in the methanol and then adding the 1,1,2-trichlorotrifluoroethane. The solvent system is highly volatile, which prevents bleeding of fingerprint detail. To balance the alkalinity of some papers, a small amount of acetic acid may be added to the solution [5]. This was not done here, however. Some fingerprints were developed in the same manner using 5-methoxyninhydrin instead of ninhydrin, producing purple marks.

Fingerprint marks were subsequently sprayed with metal salt solutions prepared in the same manner as the ninhydrin solution. Prints were then incubated for 15 min under the conditions of temperature and humidity cited above. Humidity is essential for both the ninhydrin and metal salt treatment steps.

TABLE 1—*Ions in metal-RP complexes.*

Metal Ion	Electron Configuration
Na^+	closed shell
Mg^{2+}	closed shell
Al^{3+}	closed shell
K^-	closed shell
Ca^{2+}	closed shell
Sc^{3+}	closed shell
Sr^{2-}	closed shell
Cr^{3+}	open shell ($3d^3$)
Ru^{3+}	open shell ($3d^5$)
Mn^{2+}	open shell ($3d^5$)
Ni^{2+}	open shell ($3d^8$)
Cu^{2+}	open shell ($3d^9$)
Zn^{2+}	closed shell
Cd^{2+}	closed shell
Hg^{2+}	closed shell
La^{3+}	closed shell
Ce^{3+}	open shell ($4f^1$)
Nd^{3+}	open shell ($4f^3$)
Sm^{3+}	open shell ($4f^5$)
Eu^{3+}	open shell ($4f^6$)
Tb^{3+}	open shell ($4f^8$)

Fluorescence

Sample excitation used an argon-ion-laser/dye laser system (Coherent, Innova 90-6/599), with the argon-ion-laser operating in the all-lines blue-green mode and the dye laser operating between 560 and 600 nm. The fluorescences of treated fingerprints were assessed by visual inspection under the laser illumination (in a darkened room) through standard orange argon-ion-laser safety goggles when the argon-ion-laser was used, and goggles equipped with red-transmitting filters when the dye laser was used. Fluorescence observations were confined to fingerprints since it is risky to extrapolate from solution data, where solvation effects are important, to the fingerprint context.

Results and Discussion

Complexes formed with Na^+, Mg^{2+}, Al^{3+}, K^+, and Sr^{2+} showed solution and fingerprint colors similar to RP and yielded no fingerprint fluorescence. If one compares the absorption spectra of RP, Na-RP and Zn-RP solutions (II, Fig. 1), one finds a symmetric absorption band with maximum at 490 nm for the Zn-RP solution, but rather unsymmetrical absorption bands for Na-RP and RP solutions. In Fig. 2, the absorption spectra are plotted as $I_0 - I$, where I_0 is the incident light intensity and I the transmitted light intensity, rather than the usual optical density. It is tempting to resolve the RP and Na-RP absorption bands into two components, one with a maximum at 580 nm, the other at about 490 nm. Indeed, the Ru-RP and Cr-RP complexes exhibit two distinct absorption bands (λ_{max} = 590, 500 nm). In Cr-RP this is particularly flagrant. A colored methanol solution (pale green) is formed by $CrCl_3 \cdot 6H_2O$ itself, but its absorption is in the red and near infrared (IR). For the sample concentrations used (all comparable), the optical density (1-cm cell) was about 1 at 580 nm for RP, about 0.5 at 580 nm, and 0.5 at 500 nm for Cr-RP, and about 2.5 at 490 nm for Zn-RP. The RP complexes with Mn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, La^{3+}, and Eu^{3+} showed similar optical densities at about 500 nm and no absorption at 580 nm. Table 2 summarizes the spectral features for the most important complexes of the study.

In the fingerprint samples, all prints were developed by ninhydrin to comparable intensity. In prints treated with ninhydrin/$EuCl_3 \cdot 6H_2O$, ligand-to-Eu-energy transfer leads to Eu emission, but no ligand fluorescence was found. The Tb-RP prints also showed rare earth emission, but no ligand fluorescence. No ninhydrin developed fingerprints treated with the other rare earth ions showed rare earth or ligand fluorescence. With the
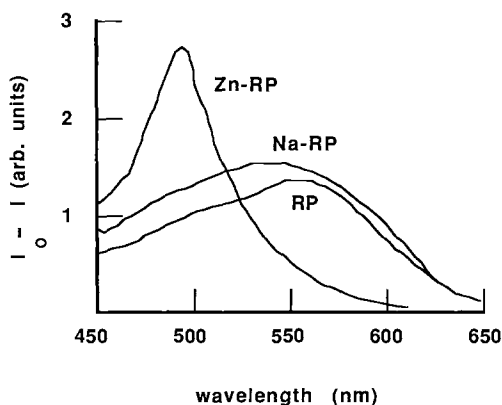

FIG. 2—*Solution absorption spectra of the Zn-RP complex, the Na-RP complex, and Ruhemann's Purple (RP).*

TABLE 2—*Spectral features of metal-RP complexes.*

Color of Complex, CH₃OH Solution	Fingerprint Color	Solution Absorbtion λ_{max}, nm	Room-Temperature Fingerprint Fluorescence
RP blue	purple	580	
K purple	purple	580	
Ca orange	violet	500	very weak orange
Sc orange	violet	500	weak yellow-orange
Cr violet	violet	590, 500	
Ru violet	violet	590, 500	
Mn orange	magenta	500	
Ni orange	orange	500	
Cu orange	red	500	
Zn yellow	yellow-orange	490	strong yellow
Cd orange	red	510	medium orange
Hg orange	pink	520	
La orange	magenta	520	weak orange
Eu orange	magenta	500	Eu emission

exception of the Europium case, all fingerprint fluorescences given in Table 2 were obtained under argon-ion-laser excitation. The rare earth emission of fingerprints treated with ninhydrin/EuCl₃·6H₂O required dye laser excitation at about 579 nm [*11*].

Metal-RP Coordination Compound Model

A structural and photophysical model has evolved from our study of metal-RP complexes. Salient background information necessary for the description of the model will be outlined first. The model will then be described and followed by interpretation of the data for metal-RP complexes in terms of this model, available X-ray structural determinations and well-established concepts of molecular spectroscopy.

Twisted Intramolecular Charge Transfer Compounds

Over 20 years ago, it was discovered that p-(N,N-dimethylamino)-benzonitrile (*IV*, Fig. 1) displays a dual fluorescence. The higher energy fluorescence band is termed "normal" based upon comparison with closely related benzene derivatives. The lower energy band is called "anomalous." The origin of the anomalous fluorescence is now understood to involve the internal twisting of the dimethylamino group, coupled with an electron transfer from the amine nitrogen to the π_*^* orbital of the benzonitrile group. The normal band does not involve such intramolecular charge transfer and has the dimethylamino and benzonitrile groups in a coplanar arrangement. Numerous compounds, many of them involving groups that can rotate about a nitrogen-carbon single bond, have since been shown to behave similarly, forming twisted intramolecular charge transfer (TICT) states in which chromophores are perpendicular to each other. It is now also recognized that in many such compounds the TICT state emits only weakly or not at all. A comprehensive review of TICT compounds has been given by Rettig [*12*].

Structure of Metal-RP Complexes

When one considers the structure of RP, a striking similarity to TICT compounds is noted since RP has two chromophores connected by a nitrogen-carbon single bond. It

seems reasonable to anticipate that in the excited state RP will assume a twisted config-
uration. Because the overlap of the π systems of the 1,3-indandione moieties is then
minimized, the fluorescence efficiency should be reduced. This is consistent with the
absence of fluorescence from RP itself. The X-ray structure determination [13] of the
protonated RP shows that already in the ground state the 1,3-indandione groups are far
from coplanar. An X-ray crystal structure of the Cd-RP complex [14] prepared with CdI_2
shows that RP acts as a tridentate ligand, that one I^- is bound to the Cd^{2+} ion, and that
two water molecules complete the (distorted) octahedral coordination. In the Cd-RP
complex (Va, Fig. 1), the two indandione groups are forced to be nearly coplanar [14].
This coplanar state is fluorescent. Since the stoichiometry of the zinc complex is the same
as that of the cadmium complex [14], and since zinc and cadmium have similar chemical
properties, the Zn-RP complex is presumed to have a structure (Vb, Fig 1) analogous
to that of the reported cadmium complex. The stronger fluorescence of the zinc complex
suggests that in this complex the 1,3-indandione moieties are more nearly coplanar. It
should be noted, however, that the higher atomic number of cadmium implies greater
spin-orbit coupling, which tends to quench the ligand fluorescence.

At first glance, there does not appear to be any need to invoke the existence of an
intramolecular charge transfer. It should, in principle, suffice to consider the coplanarity
of the 1,3-indandione moieties. However, this would not account for the exceptionally
strong fluorescence seen with 5-methoxyninhydrin. If one assumes an intramolecular
charge transfer role, the behavior of 5-methoxyninhydrin is readily understood. The
electron-donating methoxyl group reduces the electron acceptor strength of the
1,3-indandione moiety so that electron transfer to it from the nitrogen of the complex is
inhibited. This, in turn, reduces the tendency for the nonluminescent TICT state to form.
If one compares the absorption spectra of metal-RP complexes in methanol and in water,
a red shift is noted in the latter solvent. Red shifts with increasing solvent polarity are
often observed for TICT compounds [12].

Interpretation of Spectral Features

We interpret our data in terms of the above-described TICT model. Increasing co-
planarity of the indandione moieties, hence increasing the tendency for fluorescence to
occur, is equated with color change of the metal-RP complexes from purple to violet, to
magenta, to red, to orange, and then to yellow.

On this basis, RP complexes with Na^+, K^+, Mg^{2+}, Sr^{2+}, and Al^{3+} should not produce
fingerprint fluorescence, and none was found. With the Na-RP and K-RP complexes,
this is as expected. These ions can bind to the O^- of RP, but no other bonds will form
to force a coplanar arrangement of the indandione moieties.

On the basis of the colors of the formed complexes, one would expect the manganese,
nickel, and copper complexes to have coplanar (or nearly so) indandione moieties and
thus fluoresce. That fluorescence is absent, is readily understood, however. The Cu^{2+}
and Mn^{2+} cations each have an unpaired electron which spin-orbit couples to the ligand
system and this quenches fluorescence. This is reminiscent, for example, of the analogous
situation in the fluorescence of copper phthalocyanine [15]. Although Ni^{2+} is diamagnetic,
neither nickel porphyrin or nickel phthalocyanine show fluorescence because in open-
shell complexes d-π interactions effectively quench fluorescence. The same interpretation
is made here for Ni-RP. Analogous considerations apply to the rare earth-RP complexes,
none of which showed ligand fluorescence when fingerprints were treated. The La-RP
complex, however, did yield an orange fingerprint fluorescence, albeit a fairly weak one.
On the basis of its color, it should have nearly coplanar indandione moieties. Although
La^{3+} has a closed-shell configuration, it also has a fairly high atomic number, which would
produce spin-orbit coupling (heavy atom effect). Therefore, it is not surprising that the
La-RP complex fluoresces only weakly.

The Hg-RP complex did not exhibit room-temperature fingerprint fluorescence. This complex yielded pink fingerprints, a color that suggests considerable deviation from coplanarity of the indandione moieties. Moreover, mercury has a high atomic number. The absence of room-temperature fingerprint fluorescence is therefore not surprising. Successively greater deviation from coplanarity in the RP complexes with zinc, cadmium, and mercury is in line with the decrease in molar extinction coefficients (about 57 500, 37 000, 27 000, respectively) reported by Lennard and co-workers [14]. The extinction coefficient reported by the authors for RP was 20 000. Our solutions showed similar relative optical densities.

On the basis of the colors of Ca-RP and Sc-RP in solution, these complexes should produce fingerprint fluorescence. For developed fingerprints, however, the colors obtained indicate considerable deviation from coplanarity, implying that solvation plays an important role in the structure of these complexes. That (weak) Ca-RP and Sc-RP fingerprint fluorescence is observed, even though the violet color suggests considerable deviation from coplanarity, can nonetheless be understood in terms of the closed shell electron configuration and the low atomic numbers of cadmium and scandium, which would make spin-orbit coupling-induced fluorescence quenching less important than in the complexes with metals of higher atomic number.

Figure 3 gives a pictorial summary of the fluorescence features of the zinc, cadmium, and scandium complexes with RP and the 5-methoxy analog (fingerprints on paper). Several comments need to be made about this fluorescence photograph (taken under blue-green argon-ion-laser excitation through a standard orange argon-ion-laser safety filter transmitting at wavelengths longer than about 550 nm). The zinc complex with the 5-methoxy analog of RP fluoresced so strongly that the film was grossly overexposed by the fluorescent print (top left). The corresponding cadmium complex (third from left, top row) yielded clearly much weaker emission. The observations with RP (second versus fourth, top row) are analogous. Orange Cd-RP fluorescence is present. There is also
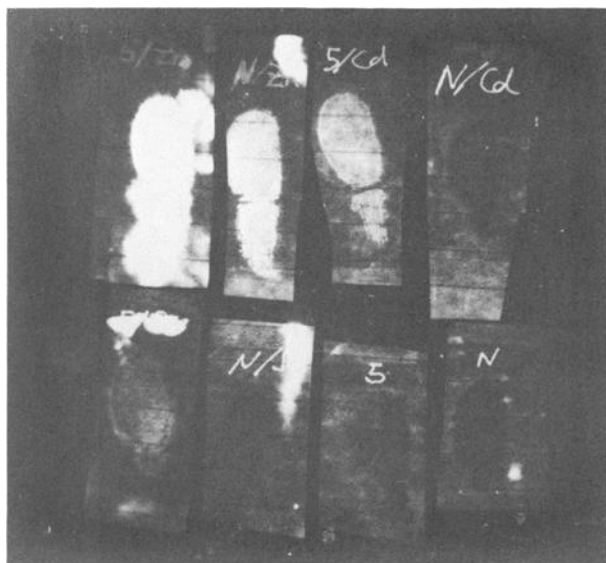

FIG. 3—*Fluorescence of fingerprints treated first with 5-methoxyninhydrin (5) or ninhydrin (N) and then with Zn, Cd, or Sc salts.* Top, left to right: *5/Zn, N/Zn, 5/Cd, N/Cd.* Bottom, left to right: *5/Sc, N/Sc, 5, N. See text for discussion.*

substantial yellow paper fluorescence, however, so that in the black-and-white photograph the Cd-RP fluorescence is masked. The same situation pertains to the scandium case (left versus second from left, bottom row). RP and its 5-methoxy analog (bottom row right and second from right) yielded no emission.

Summary

The essential features of the proposed model to explain the structural and photophysical features of metal-RP coordination compounds are

1.   In the coordination compounds, the 1,3-indandione moieties must be nearly coplanar for fluorescence to occur.
2.   When these moieties are not coplanar, a non-emitting TICT state is formed.
3.   The metal ion's ability to form a coordination compound in which RP acts as a tridentate ligand is essential, as is a closed shell electron configuration. A low metal atomic number is also helpful.
Several predictions can be made on the basis of this model, namely:

a.   It will be difficult to find a coordination compound superior to Zn-RP (or the corresponding complexes formed using ninhydrin analogs).
b.   Strongly electron donating substituents, akin to the 5-methoxyl group in 5-methoxyninhydrin, may yield increased fluorescence of metal-RP complexes. Substituted benzo(f)ninhydrins should be explored. We are beginning to work in this area.
c.   If one wishes to take advantage of intramolecular energy transfer to luminescent rare earths, ninhydrin analogs can be designed to optimize the ligand-rare earth spectral overlap and energy transfer efficiency. We are currently working in this area also.

An issue unresolved by the model in its present form is that fingerprint treatment with 5,6-dimethoxyninhydrin or benzo(e)ninhydrin [7], when followed by $ZnCl_2$ treatment and laser examination, does not yield fluorescence. Perhaps steric hindrance effects or repulsion effects due to high electron density on the indandione groups play a role here. The RP analogs may be so strongly twisted in the ground state that coordination compounds cannot form, or, if they do, the deviation from indandione coplanarity remains large.

Acknowledgment

References

[1]   Ruhemann, S., "Triketohydrindene Hydrate," *Journal of Chemical Society*, Vol. 97, 1910, pp. 2025–2031.
[2]   Oden, S. and von Hofsten, B., " Detection of Fingerprints by the Ninhydrin Reaction," *Nature (London)*, Vol. 173, 1954, pp. 449–450.
[3]   Dalrymple, B. E., Duff, J. M., and Menzel, E. R., "Inherent Fingerprint Luminescence— Detection by Laser," *Journal of Forensic Sciences*, Vol. 22, No. 1, Jan. 1977, pp. 106–115.
[4]   Menzel, E. R., *Fingerprint Detection with Lasers*, Marcel Dekker, New York, 1980.
[5]   Herod, D. W. and Menzel, E. R., "Laser Detection of Latent Fingerprints: Ninhydrin Followed by Zinc Chloride," *Journal of Forensic Sciences*, Vol. 27, No. 2, April 1982, pp. 513–518.

[6] Everse, K. E. and Menzel, E. R., "Sensitivity Enhancement of Ninhydrin-Treated Latent Fingerprints by Enzymes and Metal Salts," *Journal of Forensic Sciences*, Vol. 31, No. 2, April 1986, pp. 446–454.

[7] Almog, J., Hirshfeld, A., and Klug, J. T., "Reagents for the Chemical Development of Latent Fingerprints: Synthesis and Properties of Some Ninhydrin Analogues," *Journal of Forensic Sciences*, Vol. 27, No. 4, Oct. 1982, pp. 912–917.

[8] Menzel, E. R. and Almog, J., "Latent Fingerprint Development by Frequency-Doubled Neodynium: Yttrium Aluminum Garnet (Nd:YAG) Laser Benzo(f)ninhydrin," *Journal of Forensic Sciences*, Vol. 30, No. 2, April 1985, pp. 371–382.

[9] Almog, J. and Hirshfeld, A., "5-Methoxyninhydrin: A Reagent for the Chemical Development of Latent Fingerprints That is Compatible with the Copper-Vapor Laser," *Journal of Forensic Sciences*, Vol. 33, No. 4, July 1988, pp. 1027–1030.

[10] Stoilovic, M., Kobus, H. J., Margot, P. A., and Warrener, R. N., "Improved Enhancement of Ninhydrin Developed Fingerprints by Cadmium Complexation Using Low-Temperature Photoluminescence Techniques," *Journal of Forensic Sciences*, Vol. 31, No. 2, April 1986, pp. 432–445.

[11] Menzel, E. R. and Mitchell, K. E., "Intramolecular Energy Transfer in the Europium-Ruhemann's Purple Complex: Application to Latent Fingerprint Detection," *Journal of Forensic Sciences*, Vol. 35, No. 1, Jan. 1990, pp. 35–45.

[12] Rettig, W., "Charge Separation in Excited States of Decoupled Systems-TICT Compounds and Implications Regarding the Development of New Laser Dyes and the Primary Processes of Vision and Photosynthesis," *Angewandte Chemie, International Edition in English*, Vol. 25, 1986, pp. 971–988.

[13] Grigg, R., Malone, J. F., Mongkolaussavaratana, T., and Thianpatanagul, S., "Cycloaddition Reactions Relevant to the Mechanism of the Ninhydrin Reaction. X-Ray Crystal Structure of the Protonated Ruhemann's Purple, A Stable 1,3-Dipole," *Journal of the Chemical Society, Chemical Communications*, 1986, pp. 421–422.

[14] Lennard, C. J., Margot, P. A., Sterns, M., and Warrener, 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.

[15] Vincett, P. S., Voigt, E. M., and Rieckhoff, K. E., "Phosphorescence and Fluorescence of Phthalocyanines," *Journal of Chemical Physics*, Vol. 55, 1971, pp. 4131–4140.

Address requests for reprints or additional information to
Dr. E. Roland Menzel
Physics Department
Texas Tech University
Box 4270
Lubbock, TX 79409