

## Synthesis, identification and analytical properties of the 2-pyridilideniminobenzohydroxamic acid

F SÁLINAS\*, M JIMÉNEZ-ARRABAL and I DURÁN MERÁS  
Department of Analytical Chemistry, Faculty of Sciences, University of Extremadura,  
06071 Badajoz, Spain

MS received 25 November 1985; revised 23 April 1986

**Abstract.** 2-Pyridilideniminobenzohydroxamic acid (PIBHA) has been synthesized by the reaction of *o*-aminobenzohydroxamic acid and pyridine-2-carbaldehyde. Its solubility in several solvents, spectral characteristics and  $pK_a$  values are reported. Its reactivity with inorganic ions, in aqueous media and by extraction with chloroform, isoamyl alcohol, toluene, and a toluenic solution of trioctylmethylammonium chloride (Adogen 464) has been investigated. The  $pK$  values corresponding to the formation constants of the complexes formed between PIBHA and Cd(II), Mn(II), Co(II), Ni(II) and Cu(II) in ethanol-water medium are also reported.

**Keywords.** 2-Pyridilideniminobenzohydroxamic acid; physicochemical properties; analytical properties; formation constants.

### 1. Introduction

Hydroxamic acids constitute a group of analytical reagents frequently used (Brandt 1960; Bass and Yoe 1966; Majumdar 1971; Bhaduri 1956; Poddar *et al* 1966; Agrawal 1980; Agrawal and Patel 1980), however, between the numerous used derivatives, the azomethinic group is rarely found. This group endows a good reactivity to Schiff bases, another important group of analytical reagents (Jungreis and Thabet 1969).

Among this kind of reagents we know the use of the 2-salicylideniminobenzohydroxamic acid as an indicator in the complexometric titration of Fe(III) (Springer and Kopecka 1984), its reactivity as well as the reactivity of 2-benzylideniminobenzohydroxamic acid with inorganic ions, and some of their applications as spectrophotometric reagents (García Martín 1985; Salinas *et al* 1986b).

Data about the synthesis, analytical properties and spectrophotometric determination of iron with thienylmethylene-2-iminobenzohydroxamic acid are reported (Salinas *et al* 1986a).

In this paper, the synthesis, properties and analytical aspects of 2-pyridilideniminobenzohydroxamic acid (PIBHA, I) are reported. This compound has in its structure the azomethinic and hydroxamic groups in proper positions to intervene simultaneously in the formation of chelates with inorganic ions. Also, this compound has an N pyridinic group. So, we expect it to have an improved chelating ability.

---

\* To whom all correspondence should be addressed.

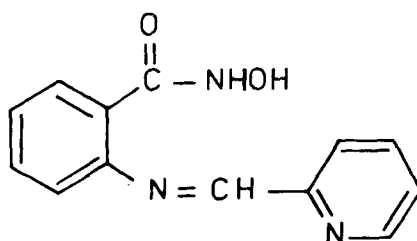


Chart 1.

## 2. Experimental

### 2.1 Reagents and apparatus

All solvents and chemicals used were of analytical grade. Stock solutions of the metals were standardized by well-known methods. Deionized water was employed for all purposes. Infrared spectra were recorded with a Perkin-Elmer 339 IR spectrophotometer in the  $4000\text{--}400\text{ cm}^{-1}$  range, using the KBr pellet technique. The absorption spectra of solutions were obtained using a Beckman 25 UV-VIS spectrophotometer (1 cm quartz cells). pH measurements were carried out with a Crison Digit 501 pH-meter equipped with a glass-calomel combination electrode. The solubility of PIBHA in several solvents, was measured by the method of Wittemberger (1950) at  $25 \pm 0.1^\circ\text{C}$ . To determine the dissociation constants of PIBHA, the potentiometric methods of Schwarzembach *et al* (1947), in several proportions of ethanol, and Irving and Rossotti (1954), and the spectrophotometric method described by Wilson and Lester (1963), were applied. To determine the formation constants of the complexes formed between PIBHA and several inorganic ions in ethanol-water (1 : 1) medium, the potentiometric methods of Irving and Rossotti (1954), Bjerrum (1941) and Chaberek and Martell (1952) were applied.

### 2.2. Synthesis of PIBHA

PIBHA was synthesized by condensation of orthoaminobenzohydroxamic acid and pyridine-2-carbaldehyde. Orthoaminobenzohydroxamic acid (5 g), synthesized employing Blatt's method (Blatt 1963) was taken in a hot mixture of ethanol : water (25 : 50, v/v) and 3.15 ml of pyridine-2-carbaldehyde was slowly added. The solution was kept stirred and warm for a few minutes. After cooling a yellow solid precipitated. The product was filtered and purified by recrystallisation from water : ethanol (2 : 1, v/v) to obtain a yellowish white product (m.p.  $139 \pm 1^\circ\text{C}$ ). Elemental analysis – found: C, 64.86%; H, 4.65%; N, 17.32%. Calculated: C, 64.71%; H, 4.60%; N, 17.42%; for  $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3$ .

## 3. Results and discussion

### 3.1 Physicochemical properties of PIBHA

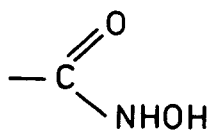
3.1a *Spectral characteristics*: The most important IR bands of PIBHA are summarized in table 1. The stretching vibration frequency of the NH group ( $3220\text{ cm}^{-1}$ )

**Table 1.** Spectral properties of PIBHA.

Infrared		Ultraviolet		
Vibration mode	Frequency (cm <sup>-1</sup> )	Solvent	λ Maxima	ε(lmol <sup>-1</sup> cm <sup>-1</sup> )
ν NH	3220 <i>s</i> *	Water	228 nm, λ <sub>1</sub>	16,02 × 10 <sup>3</sup>
ν C=O (amide I band)	1620 <i>s</i>		335 nm, λ <sub>2</sub>	2,40 × 10 <sup>3</sup>
ν OH hydroxamic	2850 <i>w</i>	ClCH <sub>3</sub>	250 nm, λ <sub>1</sub>	9,23 × 10 <sup>3</sup>
ν OH phenolic	3080 <i>s, b</i>		335 nm, λ <sub>2</sub>	2,50 × 10 <sup>3</sup>
δ NH (amide II band)	1570 <i>w</i>	Ethanol	235 nm, λ <sub>1</sub>	11,90 × 10 <sup>3</sup>
ν C-N (amide III band)	1290 <i>m</i>		335 nm, λ <sub>2</sub>	2,75 × 10 <sup>3</sup>
ν NO	955 <i>m</i>	Isoamyl alcohol	240 nm, λ <sub>1</sub>	8,85 × 10 <sup>3</sup>
			340 nm, λ <sub>2</sub>	2,86 × 10 <sup>3</sup>

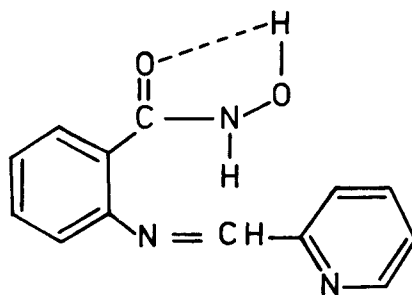
\* Abbreviations: *s* = strong; *m* = medium; *w* = weak and *b* = broad.

and the amide II band (1570 cm<sup>-1</sup>) are analogous to that of the NH group of N-substituted amides and secondary amines (Davies *et al* 1955; Miyazawa *et al* 1956; Rao and Venkataraghavan 1962). Accordingly, it is possible to affirm that PIBHA has, in the solid state, the “keto” structure, *1a*, being similar to other hydroxamic acids (Exner 1968; Bracher and Small 1970; Larsen 1978; Salinas *et al* 1982).

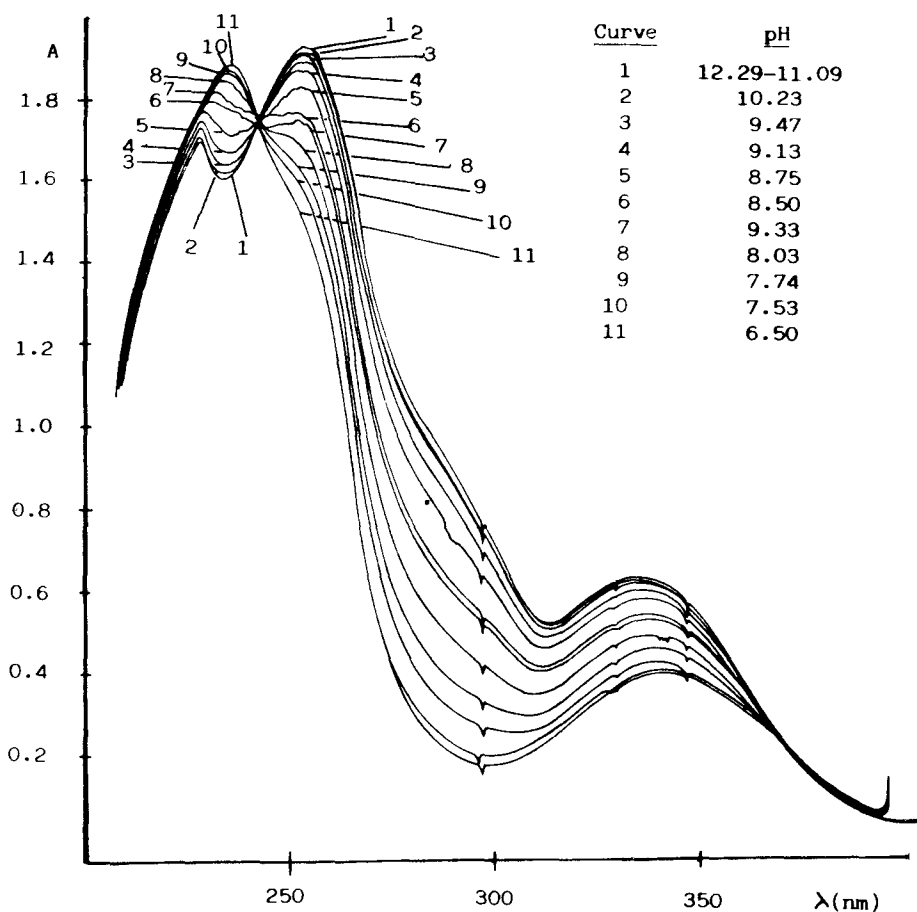


**Chart 1a.**

Since the stretching frequency of the free NH group appears around 3400 cm<sup>-1</sup>, the decrease for PIBHA, as well as for other hydroxamic acids (Mathis 1961) can be attributed to the formation of hydrogen bonding. This point is also confirmed by observing the vibrational frequencies due to CO (1600 cm<sup>-1</sup>); OH (phenolic, 3180 cm<sup>-1</sup>) and OH (hydroxamic, 2850 cm<sup>-1</sup>). The low frequency of these bands indicates hydrogen bonding (Hadži and Prevorsek 1957; Mathis 1961; Agrawal and Roshama 1978). Thus, it is concluded that the structural type II represents the most probable configuration of PIBHA.



**Chart 2.**

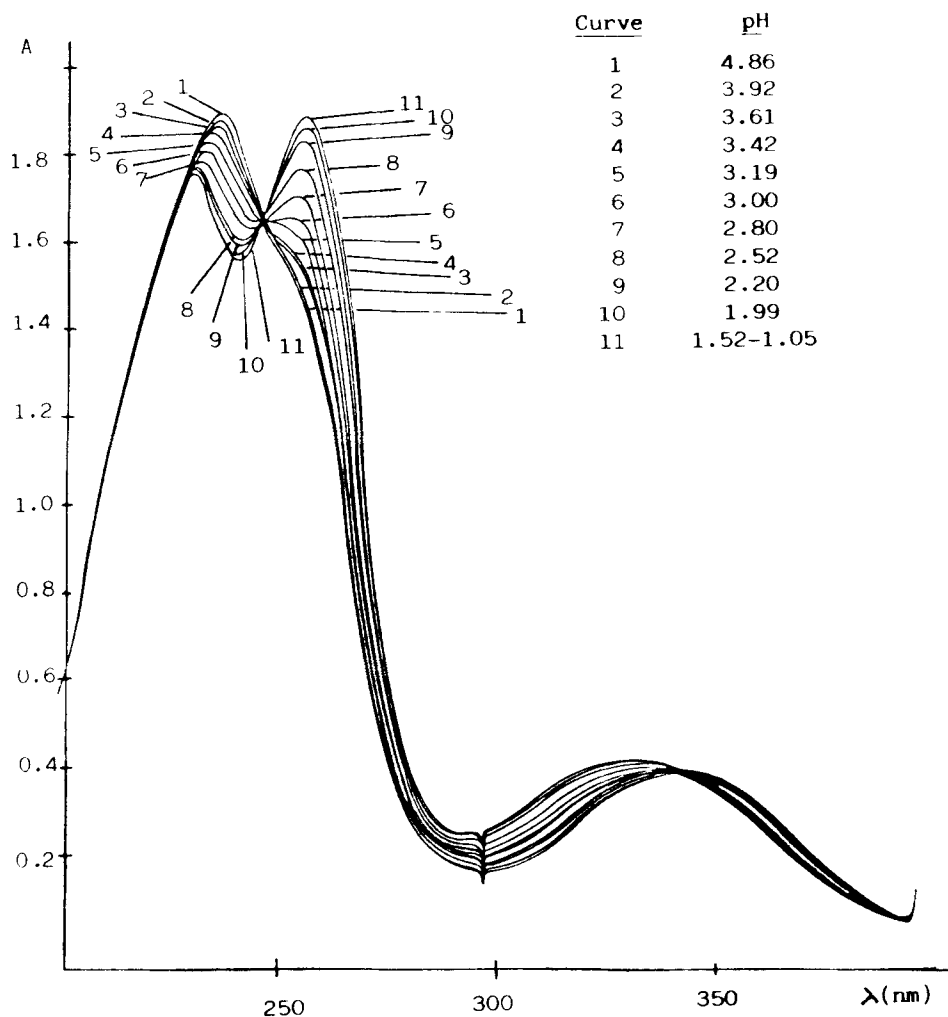


**Figure 1.** Variation of the absorption spectra of PIBHA for values of pH between 12.29 and 6.50.  $[\text{PIBHA}] = 1.66 \times 10^{-4} \text{ M}$ ,  $[\text{KCl}] = 0.1 \text{ M}$ .

The absorption maxima of PIBHA and their molar absorptivities ( $\epsilon$ ) in aqueous, ethanolic, isoamyl alcohol and chloroform solutions are given in table 1.

The absorption spectrum of PIBHA in aqueous solution shows a remarkable pH dependence. In the pH range of 12 to 6 (figure 1), the absorption maximum at 235 nm shows hyperchromic and bathochromic effects as the pH is decreased. At the same time, the maximum at 255 nm shows hypochromic and hypsochromic effects, while the maximum at 300 nm shows a hypochromic effect. Finally, one isosbestic point appears at 242 nm. This isosbestic point is indicative of the existence of two acid-base equilibrium forms that must correspond to the dissociation of the hydroxamic group and to the corresponding keto-enolic equilibrium.

In the pH range of 5-1.05 (figure 2), the maximum at 235 nm reveals hypsochromic and hypochromic effects as the pH is decreased, the maximum at 255 nm shows hyperchromic and hypsochromic effects, while the maximum at 330 nm is not affected. Finally, in this range of pH, two isosbestic points appear at 246 nm and 340 nm.



**Figure 2.** Variation of the absorption spectra of PIBHA for values of pH between 4.9 and 1.05.  $|\text{PIBHA}| = 1.66 \times 10^{-4} \text{ M}$ ,  $|\text{KCl}| = 0.1 \text{ M}$ .

**3.1b Solubility of PIBHA in several solvents:** The solubility of PIBHA in several solvents, was studied at  $25 \pm 0.1^\circ\text{C}$  and the results obtained indicate that PIBHA is relatively soluble in ethanol and in methylisobutylketone ( $7.4 \text{ g l}^{-1}$  and  $1.8 \text{ g l}^{-1}$  respectively) and sparingly soluble in chloroform and deionized water ( $0.6 \text{ g l}^{-1}$  and  $0.2 \text{ g l}^{-1}$  respectively).

**3.1c Dissociation constants:** Table 2 presents the values of the dissociation constants of PIBHA obtained in aqueous and ethanol-water media.

The  $pK_1$  and  $pK_2$  values can be assigned to the dissociation of the protonated N of the azomethinic group and to the protonated N pyridinic group respectively. The  $pK_3$  can be assigned to the dissociation of the NH group in accordance with the characteristic N-acid of the hydroxamic group (Deshpande and Jahagirdar 1977).

Table 2. Dissociation constants of PIBHA in different media (mol l<sup>-1</sup>).

	Ethanol-water				Reference		
	Water	100%	80-20%	70-30%		60-40%	50-50%
$pK_1$		2.00	2.15	2.12	2.08	2.04	Schwarzembach <i>et al</i> (1947)
$pK_2$		2.70	2.30	2.35	2.40	2.45	Schwarzembach <i>et al</i> (1947)
$pK_3$		8.32* ± 0.08	—	—	—	—	Wilson and Lester (1963)
		8.19† ± 0.01	—	—	—	—	Irving and Rossotti (1954)
		—	—	—	—	9.25	Irving and Rossotti (1954)

\* Average of the results obtained at 340 nm, 255 nm and 235 nm; † average of two determinations.

Table 3. Reactions of PIBHA with metallic ions and its extraction with several solvents.

Ion	Compound used	Colour of complex	Optimum pH range	$pD$	Solvent	Optimum pH range	$pD$
Ag(I)	AgNO <sub>3</sub>	Violet	3-5	4.8	Adogen-toluene*	3-5	4.0
Mn(II)	Mn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	White	3-5	3.7	—	—	—
Hg(II)	Hg(NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	White	7-9	3.0	Adogen-toluene*	5-9	3.0
Ni(II)	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Green-yellow	3-5	4.0	—	—	—
Cd(II)	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	White	3-5	4.0	—	—	—
Co(II)	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Light yellow	3-7	4.0	—	—	—
Cu(II)	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Yellow	3-7	5.0	Isoamyl alcohol	3-5	5.0
Fe(II)	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Red	3-5	5.5	Chloroform	3-5	5.0
Fe(III)	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Red	3-5	5.7	Chloroform	3-5	5.7
Ti(IV)	TiCl <sub>4</sub>	Yellow	3-5	5.5	Isoamyl alcohol	3-5	5.5
V(V)	NH <sub>4</sub> VO <sub>3</sub>	Brown	3-5	5.5	Isoamyl alcohol	3-5	5.7
Mo(VI)	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O	Yellow	3-5	5.0	Isoamyl alcohol	1-3	5.4
W(VI)	Na <sub>2</sub> WO <sub>2</sub> ·2H <sub>2</sub> O	Yellow	1-5	4.7	—	—	—

\* Toluene solution of trioctylmethylammonium chloride (Adogen 464) 1 g l<sup>-1</sup>

### 3.2 Chelating properties of PIBHA

3.2a *Reactions of PIBHA with 54 metal ions in aqueous medium:* The complex-formation reactions of PIBHA with metal ions at different pH values, are summarized in table 3. The pH range over which the sensitivity was maximum for each metal ion and their detection limits (*pD*) are also shown in the same table. Reaction has been observed only with 13 of these metal ions. Almost in all cases the respective complex compounds were precipitated, except those of Co(II) and Cu(II). Coloured solutions were obtained only with Fe(III) and Fe(II) in strongly acidic medium.

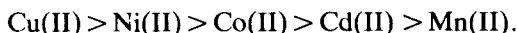
Only 8 reactions have *pD* values between 4.5 and 6, the sensitivity of the reactions is generally not high. The ions whose reactions are the most sensitive are Fe(III), Fe(II), Ti(IV), V(V) and all of these have been observed in acetic medium.

Similar reactions are observed with 2-benzylideniminobenzohydroxamic and 2-salicylideniminobenzohydroxamic acids (García Martín 1985). These reagents produce reactions, with detection limits *pD* > 4, with the ions Sn(II), La(III), Bi(III), In(III), Y(III), Al(III), Ga(III) and Ce(IV) in acetic and neutral media in addition to the reactions with PIBHA.

3.2b *Extraction of the complexes:* The observed colour reactions, after extraction into CHCl<sub>3</sub>, isoamyl alcohol, toluene and a toluenic solution of Adogen 464, are given in table 3. Only 8 ions were found to be extracted indicating that the selectivity of PIBHA can be improved by resorting to extraction. The sensitivities are of equal order, with *pD* values varying between 5 and 6, the more sensitive reactions being with Fe(III), Ti(IV), V(V) and Mo(VI). In a previous paper (Salinas *et al* 1985), the references of the extraction of hydroxamic acids complexes with inorganic ions have been summarized. The colour of the solutions and the pH range in which they are produced, are in good agreement with those observed with PIBHA.

### 3.3 Determination of the formation constants of the complexes

In table 4 the values of the formation constants of the complexes between PIBHA and Co(II), Cd(II), Ni(II), Mn(II) and Cu(II) are given. These values show that ease of formation of the complexes is in the following sequence:



This is in accordance with the values suggested by Irving and Williams (1948) for complexes between metal divalent ions and chelates with N as a donor atom.

**Table 4.** Determination of the formation constants of the complexes at 25 ± 0.1°C and in ethanol : water medium (50 : 50%, v/v)

	log <i>K</i> <sub>1</sub>	log <i>K</i> <sub>2</sub>
Cu(II)	8.50	7.71
Ni(II)	7.19	6.15
Co(II)	6.71	5.80
Cd(II)	5.91	4.95
Mn(II)	5.08	4.09

### Acknowledgements

We thank the Comisión Asesora de Investigación Científica y Técnica del Ministerio de Educación y Ciencia de España for supporting this study (Project No. 2903-83).

### References

- Agrawal Y K 1980 *Rev. Anal. Chem.* **4** 4  
Agrawal Y K and Patel S A 1980 *Rev. Anal. Chem.* **5** 1, 2  
Agrawal Y K and Roshama R 1978 *J. Chem. Eng. Data* **23** 259  
Bass V C and Yoe J C 1966 *Talanta* **13** 735  
Bhaduri A S 1956 *Z. Anal. Chem.* **151** 109  
Bjerrum J 1941 *Metal amine formation in aqueous solution* (Copenhagen: P Haase and Soon)  
Blatt A 1963 *Organic syntheses* (New York: John Wiley)  
Bracher B H and Small R W H 1970 *Acta Crystallogr.* **B26** 1705  
Brandt W W 1960 *Rec. chem. prog.* **21** 159  
Chaberek S and Martell A E 1952 *J. Am. Chem. Soc.* **74** 5052  
Davies M, Evans J C and Lumley Jones R 1955 *Trans. Faraday Soc.* **51** 761  
Deshpande R G and Jahagirar D V 1977 *J. Inorg. Nucl. Chem.* **39** 1385  
Exner O 1968 *Dansk. tidskr. farm.* **42** 145  
García Martín J P 1985 *Analytical applications of 2-benzylideniminobenzohydroxamic and 2-salicylideniminobenzohydroxamic acids* Ph. D. thesis, University of Extremadura, Badajoz, Spain  
Hadži D and Prevorsek 1957 *Spectrochim. Acta* **10** 38  
Irving H M and Rossotti H S 1954 *J. Chem. Soc.* 2904  
Irving H M and Williams R P S 1948 *Nature (London)* **162** 746  
Jungreis E and Thabet S 1969 *Chelates in analytical chemistry* (eds) H A Flaschka and A J Barnard Jr (New York: Marcel Dekker) vol. 2, pp. 149–177  
Larsen I K 1978 *Acta Crystallogr.* **B34** 962  
Majumdar A K 1971 *N-benzoylphenylhydroxylamine and its analogues* (eds) R Belcher and H Frieser (Braunschweig: Pergamon Press)  
Mathis F 1961 *Ann. Fac. Sci. Univ. Toulouse Sci. Math. Sci. Phys.* **25** 125  
Miyazawa T, Shimanovchi T and Mizushima 1956 *J. Chem. Phys.* **24** 408  
Poddar S N, Sengupta N R and Adhya J N 1966 *Indian J. Chem.* **3** 135  
Rao C N R and Venkataraghavan R 1962 *Spectrochim. Acta* **18** 273  
Salinas F, Capitán Vallvey L F and Gázquez D 1982 *Microchem. J.* **27** 188  
Salinas F, Espinosa A and Sánchez Casas J 1986a *Ann. Chim.* (in press)  
Salinas F, Mahedero M C and García Martín J P 1986b *Bull. Soc. Chim. Belg.* **95** 89  
Salinas F, Martínez-Vidal J L and González Parra J 1985 *Proc. Indian Acad. Sci. (Chem. Sci.)* **95** 265  
Schwarzembach G, Willi A and Bach R 1947 *Helv. Chim. Acta* **30** 1303  
Springer V and Kopecka B 1984 *Ceskolav Farm.* **33** 6  
Wilson R F and Lester G W 1963 *Talanta* **10** 319  
Wittemberger W 1950 *Chimische laboratoriumstechnik* 4th Edn (Vienna: Springer) p. 101