Spectral properties and reactivity of the binuclear complex ion μ-(p-benzoquinonediimine)bis[pentacyanoferrate(II)][‡]

Edgardo H. Cutín, Néstor E. Katz

Cátedra de Fisicoquímica III, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, Ayacucho 491,4000 S, M. de Tucumán, R. Argentina

Patricia A. M. Williams and Pedro J. Aymonino[§]

QUINOR, Química Inorgánica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo 962, 1900 La Plata, R. Argentina

Summary

A sodium salt containing the binuclear complex anion μ-(p-benzoquinonediimine) bis(pentacyanoferrate(II)], $[(NC)_5FeHNC_6H_4NHFe(CN)_5]^{6-}$ [first described by Herington[3]] has been isolated as a solid from an oxygenated solution of *p*-phenylenediamine and sodium amminepentacyanoferrate(II) in a 1:2 molar ratio. The i.r. and u.v.–vis. spectra point to a quinonediimine structure for the bridging ligand. In aqueous solution this ion dissociates into aquopentacyanoferrate(II) and *p*-benzoquinonediiminepentacyanoferrate(II), with $k_{obs} = 1.1 \times 10^{-2} s^{-1}$. The formation of the mononuclear pentacyanoferrate(II) complex of protonated *p*-benzoquinonediimine is favoured at pH ⩽ 8. The pK_a value for the coordinated diimine is *ca.* two orders of magnitude higher than that for the free ligand, thus indicating that *p*-benzoquinonediimine is stabilized by coordination to the $[Fe(CN)_5]^{3-}$ moiety, though to a lesser extent than in rutheniumammine analogues.

Introduction

As a continuation of our studies on mononuclear and binuclear cyanoferrate complexes[1], we became interested in *p*-benzoquinonediimine (bqd) as a bridging ligand, which may provide efficient electron communication between metal centres. This ligand, obtained by oxidation of *p*-phenylenediamine, forms intensely coloured rutheniumammine complexes[2]. A similar species is formed when *p*-phenylenediamine reacts with amminepentacyanoferrate(III) in a 1:2 molar ratio. This product has been described as the binuclear complex $[(NC)_5FeHNC_6H_4NHFe(CN)_5]^{6-}$ *(1)*, without specifying the nature of the ligand (deprotonated diamine, diimine or a free radical)[3]. Besides, this anion was isolated as a water-insoluble Zn^{2+} salt, which thus precluded reactivity studies in solution. In this work, we obtained the binuclear species by a different synthetic procedure as a water-soluble sodium salt so that its solution spectral and chemical properties could be investigated.

Results and discussion

I.r. spectrum

Figure 1 shows the i.r. spectrum of the studied salt included in a thin KBr wafer. Bands which confirm the
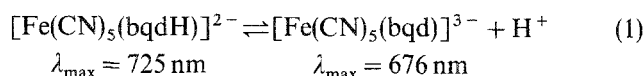
existence of imine groups are located at $3267 cm^{-1}$ (N—H stretch), $1410 cm^{-1}$ (C≡N stretch) and at $1176 cm^{-1}$ (NH def). These assignments were made by comparison with spectral data reported for the free ligand[4]. Strong bands at 2050 and $2090 cm^{-1}$ (C≡N stretch) {splitting similar to that observed for $[(NC)_5-Fe(4,4'-bipy)Fe(CN)_5]^{6-}$ (4,4'-bipy = 4,4'-bipyridine)[5]} and at $571 cm^{-1}$ (Fe—C stretch) are characteristic for cyanide bonded to iron(II)[6] [cf.[7] for $Fe^{III}CN$]. These results confirm the structure proposed for *(1)*.

Electronic spectrum

Figure 2 shows the u.v.–vis. spectrum of *(1)* in aqueous solution at pH = 10 ($NaHCO_3/Na_2CO_3$ buffer) and $C = 5.4 \times 10^{-5} M$. The observed $\lambda_{max} = 685 \pm 2 nm$ ($\varepsilon = 1.6 \times 10^4 M^{-1} cm^{-1}$ [± 5%]) agrees with the value reported by Herington[3]. This band can be assigned to a metal-to-ligand charge transfer transition (MLCT) d_π (Fe)→π* (bqd), by comparison with similar complexes, as shown in Table 1, and discussed later. The shoulder at 280 nm ($\varepsilon = 8.7 \times 10^3 M^{-1} cm^{-1}$) may be due to a π → π* transition of coordinated bqd, by comparison with reported data[2a, 8].

Kinetic and equilibrium studies

At pH = 10, *(1)* is stable in aqueous solution for at least 1 hour, but during the same period and between pH = 8 and pH = 4, the absorption maximum shifts from 685 to 725 nm, which suggests formation of the mononuclear complex, $[(NC)_5Fe(bqdH)]^{2-}$. In order to detect the simultaneous formation of the $[Fe(CN)_5(H_2O)]^{3-}$ ion, a slight excess of the scavenger 4-cyanopyridine (4-CNpy) was added to a $2 \times 10^{-5} M$ aqueous solution of the binuclear ion at pH = 7 ($NaOH/KH_2PO_4$ buffer). As shown in Figure 3a, a band at 476 nm indicates the formation of $[Fe(CN)_5(4-CNpy)]^{3-}$[9]. The MLCT band at 725 nm is reversibly shifted to 676 nm (Figure 3b) by adding 0.1M NaOH solution up to pH = 12, leading to deprotonation of the *p*-benzoquinonediimine mononuclear complex obtained as a result of dissociation of the binuclear complex at pH ⩽ 8:

$$[Fe(CN)_5(bqdH)]^{2-} \rightleftharpoons [Fe(CN)_5(bqd)]^{3-} + H^+ \qquad (1)$$
$$\lambda_{max} = 725 nm \qquad\qquad \lambda_{max} = 676 nm$$

Red shifts of the MLCT bands in pentacyanoferrate(II) complexes upon metallation or protonation of the free end of a bridging ligand are well-known phenomena[10]. This is illustrated dramatically in Table 1, which covers nearly all the visible region, and where three types of ligands are compared. The metallated adduct always

---
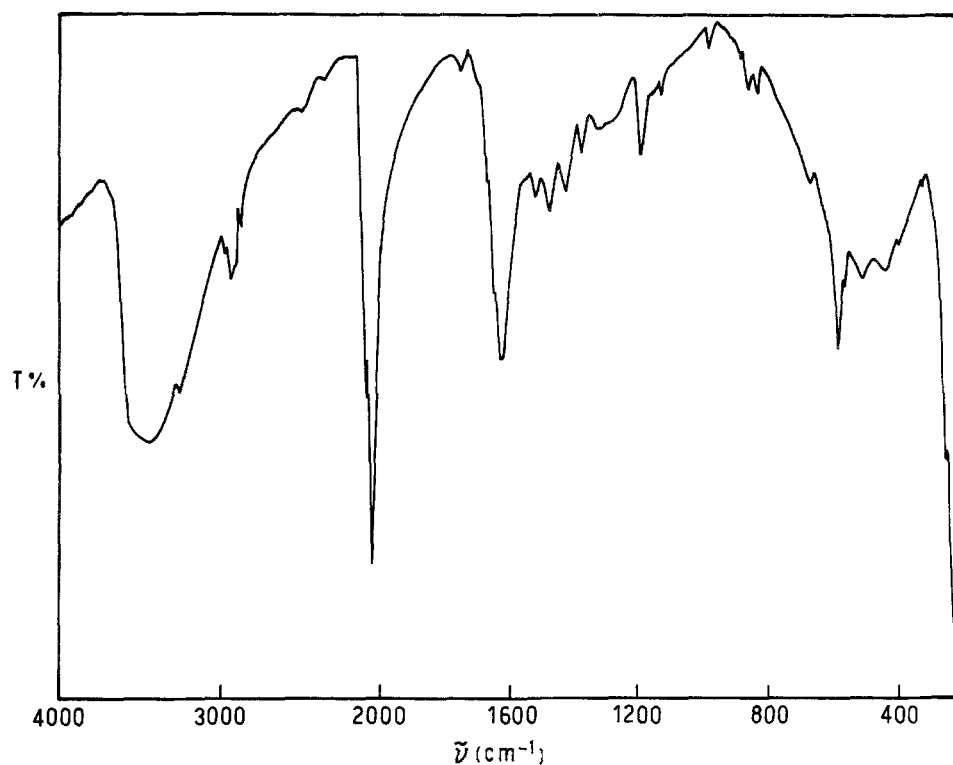
Figure 1. I.r. spectrum of $Na_6[Fe_2(CN)_{10}(bqd)]\cdot11H_2O$ (KBr pellet).

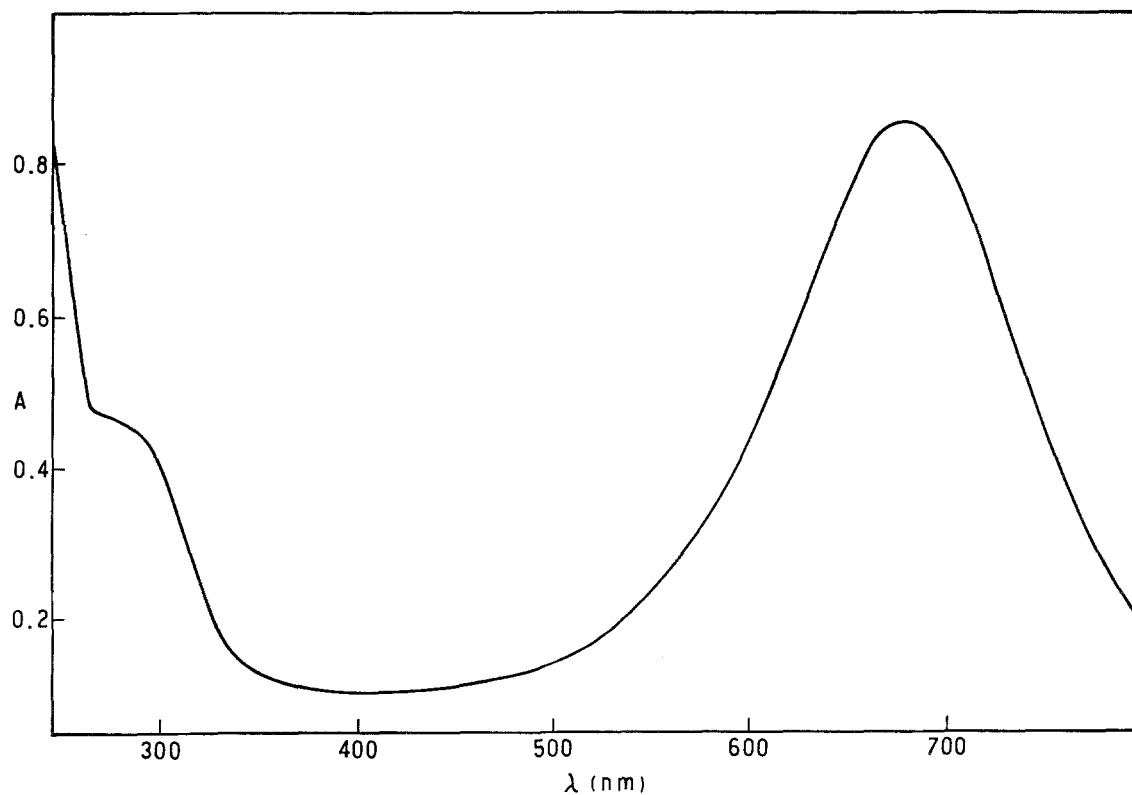**Figure 2.** U.v.–vis. spectrum of an aqueous solution $(5.4 \times 10^{-5}\,M)$ of $[Fe_2(CN)_{10}(bqd)]^{6-}$.

absorbs between the corresponding mononuclear and the protonated species. Interestingly, these quinonediimine ligand bands are assigned to LMCT (ligand-to-metal charge transfer) transitions in rutheniumammine complexes[2a], since a blue shift occur when the diimine is protonated. This striking difference can be ascribed to the lower d_π energy levels of $[Fe(CN)_5]^{3-}$ as compared to $[Ru(NH_3)_5]^{2+}$[13].

Figure 4 shows spectra obtained at different times after dissolving a mixture of *(1)* $(C = 5 \times 10^{-5}\,M)$ and 4-CNpy $(C = 4.5 \times 10^{-4}\,M)$ at pH = 7. Isosbestic points suggest a direct relationship between the two species formed from

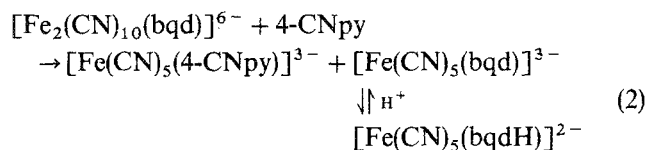**Table 1.** Electronic spectra of $[Fe(CN)_5L]^{n-}$ complexes.

L	λ_{max} (nm)	Ref.
N◯—CH₂NH₂	365	1a
N◯—CH₂NH₂Fe(CN)₅	370	1a
N◯—CH₂N⁺H₃	390	1a
N◯N	452	11
N◯NFe(CN)₅	508	12
N◯N⁺H	625	13
HN=◯=NH	676	This work
HN=◯=NHFe(CN)₅	685	3, this work
HN=◯=N⁺H₂	725	This work

the binuclear ion: $[Fe(CN)_5(bqdH)]^{2-}$ and $[Fe(CN)_5(4\text{-CNpy})]^{3-}$.

The observed rate constant, $k_{obs} = (1.1 \pm 0.2) \times 10^{-2}$ s^{-1} (25° C, I = 1 M) for the dissociation of the binuclear

species is independent of pH (between pH = 9 and 5) and seems to be much larger than the corresponding value for the mononuclear species. The increased lability of binuclear complexes as compared to mononuclear ones has been noted previously[14, 15]. The effect of decreasing pH is to displace equilibrium (1) to the left. From the changes in λ_{max}, a value of $pK_a = ca.$ 7.5 is estimated for coordinated bqd. The stoichiometry of the process can then be formulated, Equation (2):

$$[Fe_2(CN)_{10}(bqd)]^{6-} + 4\text{-CNpy}$$
$$\rightarrow [Fe(CN)_5(4\text{-CNpy})]^{3-} + [Fe(CN)_5(bqd)]^{3-}$$
$$\Updownarrow H^+ \qquad\qquad (2)$$
$$[Fe(CN)_5(bqdH)]^{2-}$$

At high pH values ($\geqslant 11$), λ_{max} shifts to 694 nm after one day, suggesting hydrolysis of bqd to *p*-benzoquinone monoimine[16]. Addition of EDTA or $FeCl_3$ to an aqueous solution of *(1)* does not modify the observed behaviour, discarding the possible interference of mixed-valence species. On the other hand, ascorbic acid causes the reduction of bqd with simultaneous disappearance of the MLCT band. This reduced complex dissociates very rapidly, the main products being scavenged by 4-CNpy.

In addition, bqd is hydrolyzed rapidly in aqueous solution[17]; this does not occur when it coordinates to $Fe(CN)_5^{3-}$. Besides, the estimated pK_a value (*ca.* 7.5) is almost two orders of magnitude larger than the free ligand value (5.75)[2a], although to a lesser extent than for the corresponding rutheniumammine complexes[2a]. This stabilization of bqd must be due to its strong π-interaction with metal centres.
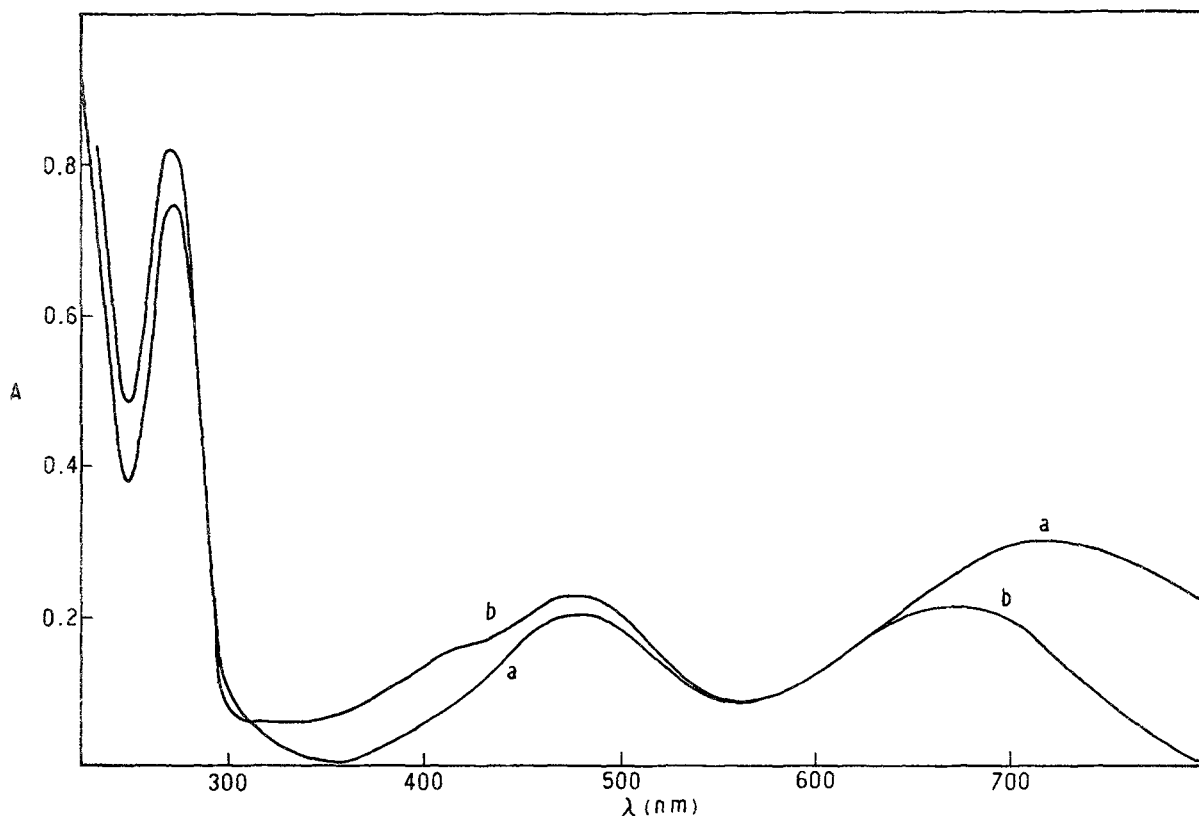

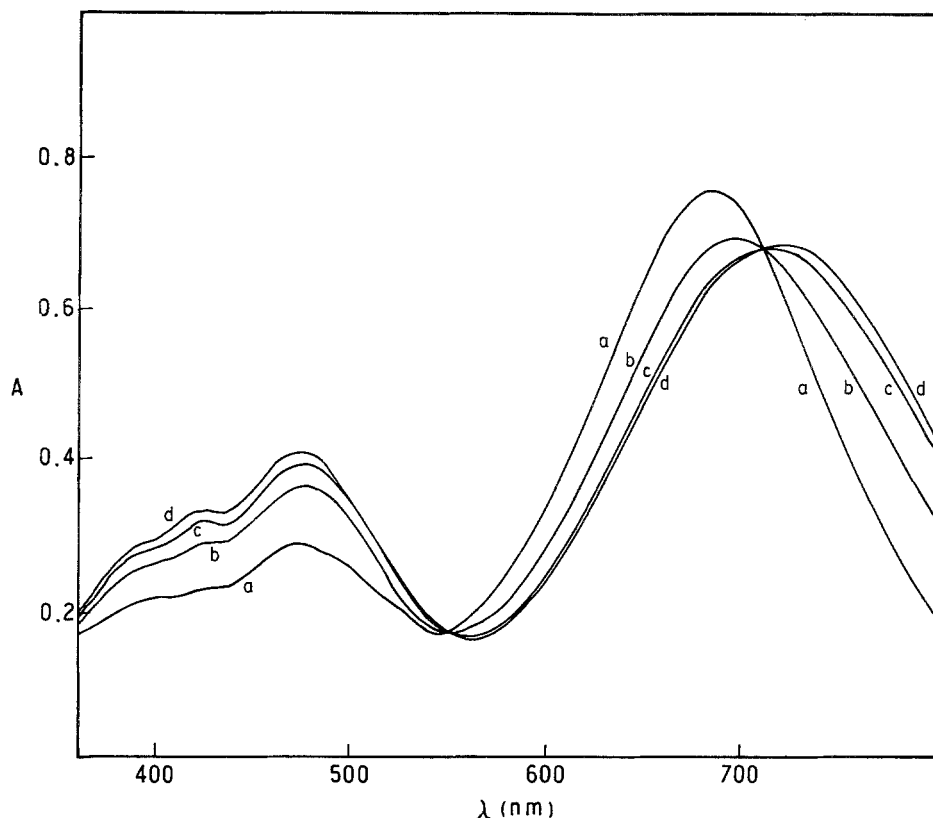**Figure 3.** U.v.–vis. spectrum of $[Fe_2(CN)_{10}(bqd)]^{6-}$ in aqueous solution with added 4-CNpy, at a) pH = 7; b) pH = 12.

Figure 4. U.v.–vis. spectrum of an aqueous solution of $[Fe_2(CN)_{10}(bqd)]^{6-}$ with added 4-CNpy at pH = 7, at a) 2 min; b) 15 min; c) 30 min; d) 80 min.

Experimental

Materials

Analytical reagents were used for all experiments reported in this work. Doubly distilled H_2O was redistilled from alkaline $KMnO_4$ in an all-glass apparatus.

Preparations

1,4-Phenylenediamine (0.21 g) (previously sublimed *in vacuo*) and $Na_3[Fe(CN)_5(NH_3)]\cdot3H_2O$ (1.3 g), obtained by the published method[18], were dissolved in 20 cm³ of triply distilled H_2O, the pH was adjusted to *ca.* 10 with 0.1N NaOH, and the solution was oxidized by vigorous bubbling of O_2 gas for 4 h. The product was precipitated with EtOH saturated with NaBr, collected in a sintered glass filter, washed with EtOH and Et_2O, and dried in a vacuum desiccator over KOH. Yield: 0.5 g (30%). Anal. (Found: C, 23.0; N, 21.2; H, 3.7; Fe, 13.5; Na, 16.6; H_2O, 26.3 $Na_6[Fe_2(CN)_{10}(bqd)]\cdot11H_2O$ calcd.: C, 23.6; N, 20.6; H, 3.4; Fe, 13.7; Na, 16.9; H_2O, 24.3%). Carbon, hydrogen and nitrogen analyses were performed at UMYMFOR Laboratories, Buenos Aires, R. Argentina. Sodium and iron analyses were made by atomic absorption spectroscopy on a Varian Techtron AA spectrometer. Water of hydration was determined by thermogravimetry with a Rigaku YGLD thermoanalyzer.

Methods

I.r. spectra were obtained as KBr pellets on a Perkin–Elmer 983 G spectrophotometer. Electronic spectra were recorded on a Perkin–Elmer Coleman 124 spectrophotometer. Kinetic experiments were carried out with a Metrolab RC 325 spectrophotometer provided with thermostatted cells. Reactions were monitored at the λ_{max} of the product ($[Fe(CN)_5(4\text{-cyanopyridine})]^{3-}$). All runs were made in duplicate at $25.0 \pm 0.2°\,C$ using adequate buffers ($NaHCO_3$/potassium dihydrogen phosphate, Na_2CO_3/HAOH and $MeCO_2H$/NaOAc). The ionic strength was maintained at 1 M with NaCl. Rate constants were determined by a linear regression method using a TK85 Microdigital computer.

References

[1] (a) P. A. M. Williams and P. J. Aymonino, *Inorg. Chim. Acta*, **113**, 37 (1986); (b) E. H. Cutín and N. E. Katz, *Polyhedron*, **6**, 159 (1987).
[2] (a) K. Rieder, U. Hauser, H. Siegenthaler, E. Schmidt and A. Ludi, *Inorg. Chem.*, **14**, 1902 (1975); (b) S. Joss, H. B. Bürgi and A. Ludi, *Inorg. Chem.*, **24**, 949 (1985).
[3] E. F. Herington, *J. Chem. Soc.*, 3633 (1959).
[4] F. E. Pritchard, *Spectrochim. Acta*, **20**, 925 (1964).
[5] P. A. M. Williams and P. J. Aymonino, *Inorg. Chim. Acta*, **113**, L17(1986).
[6] J. A. Olabe and P. J. Aymonino, *J. Inorg. Nucl. Chem.*, **38**, 225 (1976).
[7] S. del V. Alonso, C. O. Della Védova, N. E. Katz, M. A. Martínez and P. J. Aymonino, *J. Inorg. Nucl. Chem.*, **40**, 2074 (1978).

[8] J. F. Corbett, *J. Chem. Soc. (B)*, 207 (1969).

[9] N. G. del V. Moreno, N. E. Katz, J. A. Olabe and P. J. Aymonino, *Inorg. Chim. Acta*, **35**, 183 (1979).

[10] A. Haim, *Pure and Appl. Chem.*, **55**, 89 (1983).

[11] H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).

[12] F. Felix and A. Ludi, *Inorg. Chem.*, **17**, 1782 (1978).

[13] C. R. Johnson and R. E. Shepherd, *Inorg. Chem.*, **22**, 2439 (1983).

[14] A. P. Szecsy and A. Haim, *J. Am. Chem. Soc.*, **104**, 3063 (1982).

[15] G.-H. Lee, L. Della Ciana and A. Haim, *J. Am. Chem. Soc.*, **111**, 2535 (1989).

[16] F. Felix and A. Ludi, *Inorg. Chim. Acta*, **24**, L11 (1977).

[17] J. F. Corbett, *J. Chem. Soc. (B)*, 213 (1969).

[18] D. J. Kenney, T. P. Flynn and J. B. Gallini, *J. Inorg. Nucl. Chem.*, **20**, 75 (1961).