Spectrophotometric Study of Complex Formation in Copper(II) Mono-, Di-, and Tri-ethanolamine Systems

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The complex formation between Cu^{II} and mono-, di-, or tri-ethanolamine, $NH_{3-n}R_n$ ($R = CH_2CH_2OH$, n = 1—3), has been studied using visible spectroscopy at ionic strength 1.0 mol dm^{-3} and 25 °C. Ethanolamines are found to act as multidentate ligands through amino, hydroxyl, and deprotonated hydroxyl groups. The formation constants and the individual spectra of all the complex species detected between pH 2 and 12 have been obtained by least-squares fit of visible spectrophotometric titration data. As an essential aid to understanding the copper(II)–triethanolamine system, the power of u.v.–visible spectrophotometry to distinguish between monomer and dimer species was especially studied. Two new soluble complex species were identified in this system.

The co-ordination chemistry of β-aminoalcohols in aqueous solution is of interest because of their ability to form stable complex species at neutral and basic pH values.[1] Particularly interesting are the related complexes with aminosugars which have the same functional groups in the same relative positions as ethanolamines, and play important roles in biological systems, for instance in some human hormones (adrenaline, noradrenaline),[2] or in other natural compounds such as chitin and chitosan.[3] For a long time there has been some controversy[4—8] about the complexing abilities of the aminoalcohol moiety, which has been considered too weak for chelate formation in aqueous solution. Actually, alkoxide ion is a strong base in aqueous solution and it is protonated at neutral pH values, preventing complex formation. However, when this group is in an appropriate site with respect to another complexing group such as an amino group, the formation of chelate rings of five or six members is not only possible but the favoured process in aqueous solution at neutral and basic pH.

As a continuation of other studies of the complexing ability towards copper(II) ion of ethanolamines, monoethanolamine (mea), diethanolamine (dea), and triethanolamine (tea), $NH_{3-n}R_n$ ($R = CH_2CH_2OH$, n = 1—3), using potentiometry[9] and e.s.r. spectroscopy,[10,11] the present work concerns a visible spectroscopic examination. Furthermore, the related compound β-methoxyethylamine (mxa) is included for comparison. Another interesting fact which is further studied is the tendency of tea to form simultaneously monomer and dimer species, not observed for mea and dea. The dimerization of the Cu^{II}–tea complexes was demonstrated previously using a recently introduced e.s.r. titrimetric method.[12] Compared with potentiometry, spectrometric methods have a higher discriminatory power for the nature of the complex species formed, and they are also used for stability constant determinations. In this context, another objective of the present work is to test the viability of the visible spectrophotometric method and of the currently used least-squares techniques to evaluate simultaneously the formation constants and the individual spectra of the complexes detected.

Table 1. Summary of experimental conditions used in the determinations

System	Concentration range/ mol dm^{-3}		No. of spectra *	pH Range
	Cu^{II}	Ligand		
Cu^{II}–mea	0.002—0.016	0.020—0.91	58 (420—800 nm, 20)	2.1—12.3
Cu^{II}–mxa	0.004—0.01	0.43—0.82	35 (550—780 nm, 24)	4.1—13.0
Cu^{II}–dea	0.003—0.017	0.030—1.0	64 (500—820 nm, 17)	2.7—12.8
Cu^{II}–tea	0.0003—0.02	0.003—0.90	100 (400—900 nm, 26)	2.6—12.4

* In parentheses: wavelength range scanned and number of wavelengths measured.

Experimental

Materials.—The compounds KOH, NaOH, HNO_3, and KNO_3 were all analytical grade reagents (Merck or Fluka). Titrating solutions of acid and base were prepared using twice distilled CO_2-free water, and standardized using conventional acid–base titrimetric procedures [standards were potassium hydrogenphthalate for base and tris(hydroxymethyl)methylamine for acid solutions]. Stock solutions of Cu^{II} were prepared from $Cu(NO_3)_2$ (Merck extra-pure grade), and standardized iodometrically and electrogravimetrically. Monoethanolamine (mea), diethanolamine (dea), triethanolamine (tea), and β-methoxyethylamine (mxa), Fluka puriss., were used without further purification. Stock solutions of 2.0 mol dm^{-3} protonated ligand (ethanolammonium) nitrate salts were prepared by neutralization of weighed stoicheiometric amounts of the ligands with stock 2.0 mol dm^{-3} HNO_3 solution. The ionic strength of the measured solutions was kept at 1.0 mol dm^{-3} by adding, when necessary, the appropriate amount of KNO_3.

Amberlite IRA-120 resin was used in ion-exchange studies.

Apparatus.—Visible–u.v. spectra were recorded on a Beckman ACTA M-VII spectrophotometer, and on a Beckman DU-7 spectrophotometer interfaced (RS232) to an IBM personal computer. Spectra acquisition was controlled through Beckman Data Capture Software. The continuous spectrophotometric titration set-up consisted of a thermostatted titration cell and a continuous spectrophotometric flow-cell HELLMA 174QS (pathlength 1 cm) connected in a closed loop to a peristaltic pump. For measurements at very low metal ion concentrations ($< 5 \times 10^{-4}$ mol dm^{-3}), 10-cm pathlength cells were used. E.m.f. data and pH values for each spectrophotometrically measured solution were obtained from a Radiometer PHM64 pH meter using a combined Ross pH electrode (Orion 81–02). Titrant was added with a Methrom

Multidosimat E415 autoburette equipped with an Exchange Unit 10-cm^3 burette cylinder 552 with an antidiffusion burette tip. All the potentiometric assembly was controlled by a Hewlett-Packard 9816 microcomputer *via* an HP 3421A data acquisition control unit and an HP-IB interface.

Visible Spectrophotometric Titration Procedure.—The procedure implied the titration of slightly acidic solutions which contained different ligand-to-metal ratios and different concentrations of Cu^{II} and protonated ligand salts with a basic (NaOH, KOH, or ligand) solution. After each addition of titrant the pH was measured and the spectrum was taken and stored. In very basic media, the pH was changed by very small additions of a very concentrated base solution with negligible variation of the total volume.

Potentiometric Determinations.—Protonation of mxa and the copper(II) complexation with this ligand were studied potentiometrically under computer control using the same procedure as described for ethanolamines in previous work.[9]

Ion-exchange Studies.—The strong cationic exchange resin Amberlite IRA-120 was used in the assessment of the null charge of ethanolamine complexes formed under particular conditions.[5] When a solution of the mea, dea, or tea ligand was passed through the resin in its copper(II) form, a deep blue solution (in which the uncharged species predominates) was eluted. The visible spectra of these solutions were recorded for further study (see below). When the same experiment was carried out with ammonia or mxa (which form with Cu^{II} only cationic complexes, retained by the resin) the eluted solution remained colourless.

Data Treatment.—Stability constants and the spectra of individual species were obtained by least-squares fit of the experimental spectra using the computer program SQUAD.[13] This program has been modified in order to allow the study of a larger number of spectra (100 spectra), each with a maximum number of 50 absorbance readings at 50 different wavelengths. The subroutine COGSNR of the program was also modified to avoid occasional Newton–Raphson divergence in solving mass-balance equations, including the constrained procedure described previously.[14] Data obtained potentiometrically (protonation of β-mea and complex formation of this ligand with Cu^{II} were analysed with the program SUPERQUAD.[15] Calculations were carried out with both an IBM personal computer (spectra acquisition) and an IBM 370 main frame (SQUAD and SUPERQUAD programs).

Results and Discussion

Stoicheiometric coefficients of the species formed were first estimated.[10,11] From the spectra of solutions at high pH (12 for mea and dea and around 10 for tea) containing low ligand-to-metal ratios (between 1 and 5), it is deduced that the maximum number of ligand molecules added to the metal ion in the absorbing species prevailing under these particular conditions is two for mea and dea, and one for tea. At higher ligand

Table 2. Formation constants and visible spectral parameters for the studied complexes obtained by least-squares fit

System	Fit[a]	Complex[b]	log *K*[c]	λ[d]	ε[e]	pH[f]	%[g]
Cu^{II}–mea	0.007	110	4.63[h]	760	24	5.4	55
		120	8.23(4)	670	41	6.4	61
		12 − 1	0.90(6)	630	59	7.8	81
		12 − 2	−8.06(6)	590	36	11—12	99
Cu^{II}–dea	0.009	110	4.38[h]	780	26	5.0	55
		120	8.39(4)	730	37	6.2	75
		12 − 1	1.39(4)	680	75	7.7	71
		12 − 2	−6.97(4)	620	54	11—12	99
Cu^{II}–mxa	0.003	110	4.60[h]	770	18	5.8	74
		120	7.84(2)	690	37	7.2	71
		130	9.55(3)	640	67		
		13 − 1	−1.84(3)	610	48		
Cu^{II}–NH$_3$[i]		110	4.1	740	24	5.5	49
		120	7.6	680	32	6.3	53
		130	10.3	620	43	7.0	49
		140	12.4	590	60	10—12	99
Cu^{II}–tea[j]	0.019	110	4.37(1)	800	28	4.7	88
		11 − 1	−1.73(2)	750	51	7.0	72
		11 − 2	−9.45(1)	710	70	10—11	98
		22 − 2	−1.42(2)	750	142	6.6	58
		22 − 3	−9.02(7)	730	154	7.8	30
		22 − 4	−17.02(6)	710	197	9.7—10	65
		22 − 5	−28.50(5)	700	131	12.0	63
		12 − 2	−8.57(3)	640	41	11.0	79

[a] Least-squares fit given in standard deviation units of the residuals in the absorbances. [b] Stoicheiometry of the complex; *pqr* refers to Cu$_p$L$_q$H$_r$, where L = mea, dea, tea, or mxa and negative values of *r* mean deprotonation of the attached hydroxyl groups of the ligands or deprotonation of an attached water molecule. [c] Log of formation constant and its standard deviation (in parentheses) obtained by the SQUAD treatment. [d] Wavelength at the maximum of the absorption band in the calculated spectra. [e] Molar absorptivity at the maximum of the absorption band in the calculated spectra. [f] Optimum pH for maximum formation of each complex:[14] for mea, dea, NH$_3$, and mxa at a copper(II) concentration of 0.01 mol dm^{-3} and at a ligand concentration of 1.0 mol dm^{-3}; for tea at a copper(II) concentration of 0.0004 mol dm^{-3} for monomer and of 0.04 mol dm^{-3} for dimer, and at the optimum ligand-to-metal concentration ratios of 1 (species 11 − 2, 22 − 3, 22 − 4, and 22 − 5), 5 (22 − 2), 15 (11 − 1), and 25 (110 and 12 − 2). [g] Maximum concentration found using the CSMC procedure described in ref. 14. [h] The value of the stability constant was fixed for obtaining the corresponding species spectrum. [i] The values at the maximum of the absorption spectra were obtained from J. Bjerrum, C. J. Balhausen, and C. J. Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1275. [j] Values of stability constants and of species spectra obtained iteratively without simultaneous refinement of the related monomer and dimer.

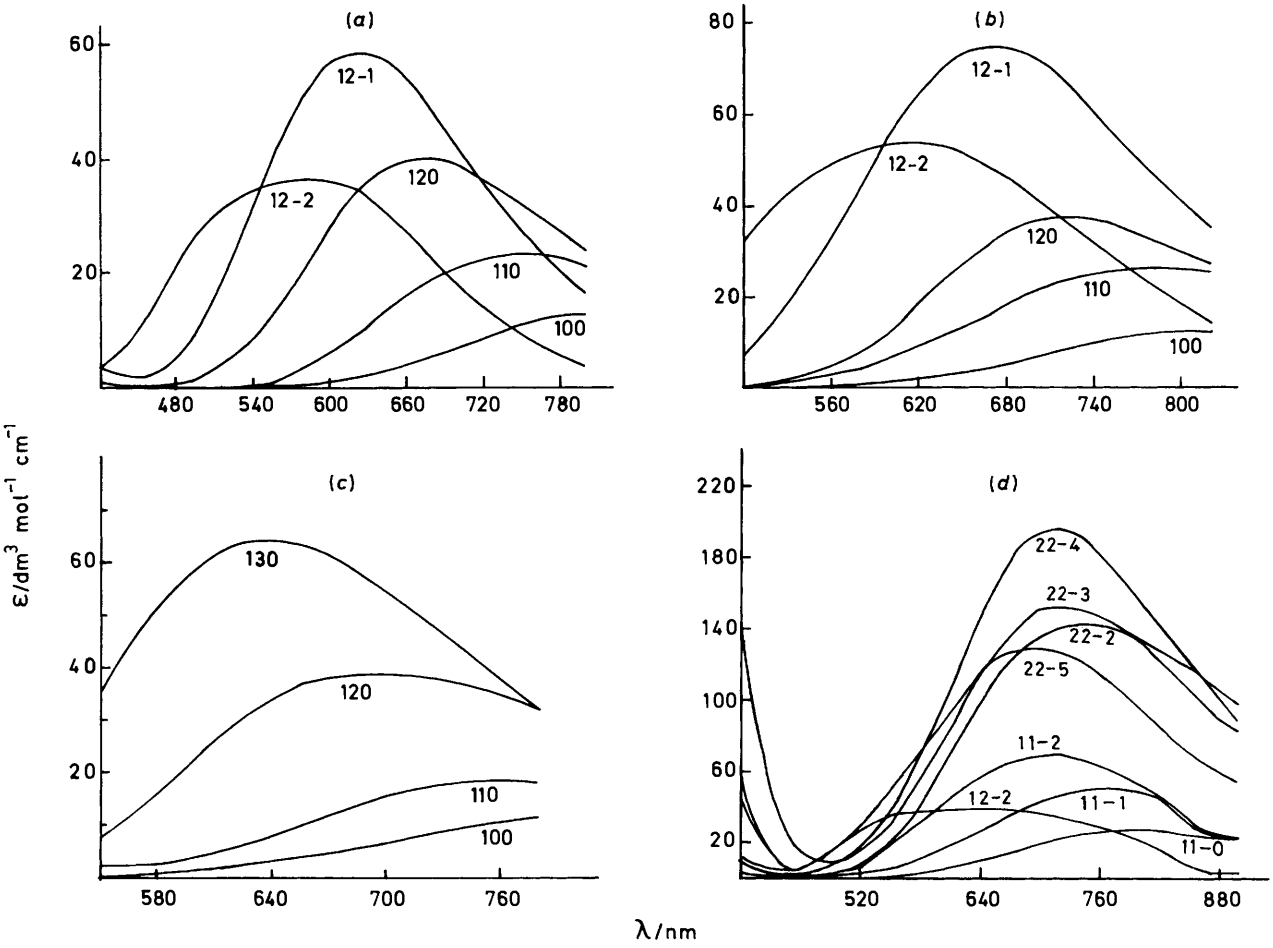

Figure. Calculated visible spectra for the different species in the systems (*a*) Cu^{II}–mea, (*b*) Cu^{II}–dea, (*c*) Cu^{II}–mxa, and (*d*) Cu^{II} tea

concentrations (1.0 mol dm^{-3}) no more ligand molecules are added in mea and dea systems, but in the tea system one complex with two molecules of ligand is formed (see below). On the other hand, the number of protons released per mol of copper ion when this is added to a ligand solution (in free amine form), evaluated from e.m.f. measurements, is two in all cases. Therefore, the stoicheiometry proposed for the mea and dea species prevailing at pH 12 is 12 – 2 (see Table 2, footnote *b* for species definition), and for tea species at pH 10 and ligand concentrations below 0.1 mol dm^{-3} is 11 – 2 or its dimer 22 – 4 (see below). At high tea concentrations (higher than 0.1 mol dm^{-3}) the prevailing species at this pH is 12 – 2. The stoicheiometries proposed for all the complexes in these systems under the assumption of stepwise formation are given in Table 2; they have been confirmed by the least-squares treatment of the experimental data.

An independent check of the stoicheiometry of the 12 – 2 species in the Cu^{II}–mea and Cu^{II}–dea systems is obtained from the spectrophotometric analysis of the deep blue solutions eluted from the cation-exchange experiments: the spectrum is very similar to that of the 12 – 2 species calculated by numerical analysis of the titrimetric spectral data (see Figure). In the 12 – 2 complex, the two ligand molecules are assumed to be chelated to the central metal ion through both amino and alkoxide groups. Conversely, in the case of mxa no neutral species is eluted after cation exchange. For tea the spectrum of the eluted solution of the neutral complex depends on the ligand concentration: when the latter is below 0.1 mol dm^{-3} the spectrum of the eluate is similar to that of the species 22 – 4, and at higher ligand concentrations the spectrum is similar to that of the 12 – 2 species.

The formation of Cu^{II}–mxa complexes requires a ligand excess larger than that used in the case of the ethanolamine systems in order to avoid the precipitation of copper(II) hydroxide. The behaviour of mxa as a ligand is similar to that of ammonia: the stepwise formation of successive ammine complexes takes place with increasing excess of the ligand. On the contrary, ethanolamines form stable complexes at basic pH even at low ratios of ligand to metal ion; at neutral pH and these low ratios, precipitation of copper hydroxide can also occur, but redissolution is achieved when the pH is raised, forming the same complex species (same e.s.r. and visible spectra) that exist in solutions with higher ligand-to-metal ratios and in which no precipitation is observed over the whole pH range.

In Table 2 the results obtained from the SQUAD least-squares numerical treatment of the experimental spectra for the four systems studied, Cu^{II}–mea, –mxa, –dea, and –tea, are summarized. The fit given refers to the standard deviation of the residuals between experimental and calculated spectra for the set of stability constants and species spectra finally proposed (see Table 2 and Figure). Since the analysed experimental data come from solutions independently prepared and from independent spectrophotometer calibration sets, the fit finally achieved is reasonably good (around 0.01 absorbance units).

When the values of the formation constants are obtained simultaneously with the individual spectra of the absorbing

Table 3. Comparison of the stepwise stability constants[a] obtained by different experimental methods

System	Complex[b]	log K from Visible spectra	 E.m.f. data[c]	 E.s.r. data[d]
Cu^{II}–mea	110	4.6	4.6	4.4
	120	3.6	3.8	4.0
	12 − 1	−7.3	−6.9	−6.9
	12 − 2	−9.0	−10.3	−9.6
Cu^{II}–dea	110	4.4	4.4	4.2
	120	4.0	3.7	3.2
	12 − 1	−7.0	−6.7	−7.2
	12 − 2	−8.4	−7.3	−8.4
Cu^{II} mxa[e]	110	4.6	4.6	4.4
	120	3.2	3.1	4.1
	130	1.7	2.1	1.9
	13 − 1	−11.4		
Cu^{II}–tea	110	4.4	4.3	4.3
	11 − 1	−6.1	−6.2	−6.3
	11 − 2	−7.7	−6.8	−7.8
	22 − 2	−5.8	−5.4	−5.4
	22 − 3	−7.6	−7.1	−7.1
	22 − 4	−8.0	−8.4	−8.4
	22 − 5	−11.5		
	12 − 2	0.9		

[a] Stepwise stability constant for the equilibrium; *e.g.* for ligand addition $Cu(L)_a + L \rightleftharpoons Cu(L)_{a+1}$, or for hydroxyl deprotonation $Cu(L)_pH_r \rightleftharpoons Cu(L)_pH_{r-1} + H^+$. [b] Same notation for stoicheiometries as in Table 2. [c] See ref. 9. [d] See refs. 10 and 11. [e] Potentiometric values for protonation (log K = 9.63) and for copper(II) complexation of mxa given were obtained in the present work.

species, some correlation problems between them can arise because either the experimental data cannot be described uniquely with only one set of constants and species spectra, or because too many parameters are refined simultaneously. For the first complex, 110, which is weakly absorbing, the value of the stability constant obtained from e.m.f. data is usually more reliable than that from spectrophotometric measurements. Conversely, the values obtained spectrophotometrically at high pH for the formation constants of the last complex 12 − 2 with either mea or dea are more reliable than those obtained potentiometrically (see Table 3). Correlation problems are hard to solve in the case of the Cu^{II}–tea complexes; the resolution of the spectra of the monomer and dimer is not directly achieved by a simple SQUAD treatment. The final values given in Table 2 and the Figure for the formation constants and the individual spectra of these species have been obtained iteratively, but without recourse to simultaneous changes of the formation constants of both members of the monomer–dimer pair; after several cycles of alternative refinement of the constants for either the monomer or the dimer complex, a global minimum which fits all the experimental data, including those from solutions with low and with high metal concentrations, is achieved. Data for e.s.r. spectroscopy furnish the best experimental approach[10–12] for solving monomer–dimer dichotomy in solution. The visible spectra of the 12 − 2 complexes with mea, dea, and tea are very similar: they show one peak and one shoulder (at 590 and 510 nm for the mea complex, at 620 and 530 nm for the dea complex, and at 640 and 560 nm for the tea complex).

For the Cu^{II}–tea complexes, the binding of a second bulky ligand molecule is sterically hindered, and, therefore, the favoured process at relatively low ligand concentrations is the deprotonation of one of the hydroxyl groups and the concomitant chelation of the metal ion yielding the 11 − 1 chelate. The easy formation of dimers in solution is explained in terms of bridge formation between two metal ions through oxygen atoms from alkoxide groups. This arrangement is not sterically hindered and is common with other oxygen-bridged copper(II) dimers whose solid structures have been proposed.[16] The dimer 22 − 2 suffer further deprotonation at increasing pH, yielding the 22 − 3, 22 − 4, and even 22 − 5 species. At very high ligand concentrations the process observed is the addition of a second ligand molecule to the 11 − 2 complex to form the 12 − 2 species.

The ligands mea and dea in solution do not form dimer species because the favoured process for the 110 complex is the further addition of a second ligand molecule, which prevents the formation of dimers. When the pH is high enough for deprotonation to occur in complex 120, chelation takes place through alkoxide oxygen atoms, yielding the complexes 12 − 1 and 12 − 2.

In Table 3 the results obtained in this work for the copper(II) complexes of ethanolamines are compared with those obtained using other experimental methods. In the present study using visible spectrophotometry, two new complexes species for the tea system, 12 − 2 and 22 − 5, are detected at higher concentrations and higher pH than those previously studied with the other methods. The comparison of the stability constants shows the reinforcement of the complexing ability of the ethanolamines with respect to ammonia due to amino–alkoxo chelation. The comparison of the species spectra demonstrates that such chelation results in considerable square-planar distortion as a consequence of the in-plane interaction. It is interesting that the observed wavelength shift caused by the aminoalkoxo moiety is comparable to that caused by formation of the bis amino complex.

Conclusions

Ethanolamines act as bidentate ligands through the amino and hydroxyl groups. Below pH 12, mono- and di-ethanolamine form four species by stepwise addition of two molecules of the ligand to the metal ion (co-ordination through N) followed by deprotonation of two hydroxyl groups and chelation. Triethanolamine behaves differently: at low ligand concentrations, only one ligand molecule is added to the metal ion followed by chelation and deprotonation of the hydroxyl groups of the ligand and further, dimerization of the monomer species; at high ligand concentrations (1.0 mol dm^{-3}) a complex with two ligand molecules is formed, which has a lower stability than those formed with two molecules of mono- and di-ethanolamine. β-Methoxyethylamine forms three species below pH 11, all of them by successive addition of ligand molecules to the metal ion, which is co-ordinated only through the N atoms.

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References

1 G. Micera, S. Deiana, A. Dessi, P. Decok, B. Dubois, and H. Kozlowski, *Inorg. Chim. Acta*, 1985, **107**, 45; J. Lerivrey, B. Dubois, P. Decok, G. Micera, J. Urbanska, and H. Kozlowski, *ibid.*, 1986, **125**, 187.
2 C. J. Hawkins and J. A. Palmer, *Aust. J. Chem.*, 1978, **31**, 1689; T. Lindgreen, R. Sillanpäa, T. Nortia, and K. Pihlaja, *Inorg. Chim. Acta*, 1983, **73**, 153.
3 R. A. A. Muzzarelli, in 'Chitin in Nature and Technology,' eds. R. A. A. Muzzarelli, Ch. Jeuniaux, and G. W. Gooday, Plenum, New York, 1985.
4 M. Cadiot, *J. Chim. Phys. Phys. Chim. Biol.*, 1963, **60**, 957.
5 C. W. Davies and B. N. Patel, *J. Chem. Soc. A*, 1968, 1824.

6 J. Bjerrum, B. W. Argawalla, and S. Refn, *Acta Chem. Scand.*, 1981, **35**, 685.

7 J. Bjerrum and P. Djurdvenic, *Acta Chem. Scand., Ser. A*, 1983, **37**, 881.

8 R. D. Hancock, *Inorg. Chim. Acta*, 1981, **49**, 145.

9 E. Casassas and R. Tauler, *J. Chim. Phys. Phys. Chim. Biol.*, 1986, **83**, 409.

10 R. Tauler, E. Casassas, M. J. A. Rainer, and B. M. Rode, *Inorg. Chim. Acta*, 1985, **105**, 165.

11 R. Tauler, E. Casassas, and B. M. Rode, *Inorg. Chim. Acta*, 1986, **114**, 203.

12 W. S. Kittl and B. M. Rode, *J. Chem. Soc., Dalton Trans.*, 1983, 409.

13 D. J. Legget, *Anal. Chem.*, 1977, **49**, 276.

14 R. Tauler and E. Casassas, *Anal. Chim. Acta*, 1988, **206**, 189.

15 P. Gans, A. Sabatini, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.

16 E. Uhlig and H. Shen, *Z. Anorg. Allg. Chem.*, 1962, **316**, 25; 1966, **346**, 21; Y. Nishida, F. Numata, and S. Kida, *Inorg. Chim. Acta*, 1974, **11**, 189; I. A. Cody, S. I. Woodburn, and R. J. Magee, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3263.

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