



COMPLEXES WITH PYRIDINE DERIVATIVES. VII.* ACETATOCOMPLEXES OF COBALT(II) AND NICKEL(II) WITH SEVERAL MONOSUBSTITUTED PYRIDINES

The preparation and properties of nineteen new complexes of the type $[M(CH_3COO)_2(x-Xpy)_y]$ ($M=Co(II)$ and $Ni(II)$; $x=2, 3$, or 4 ; $X=NH_2, OH, Cl$, or Br ; $y=2$ or 4) is reported. From the infra-red spectra three modes of acetate coordination were detected: unidentate (one complex); asymmetrical (four or five complexes) and symmetrical bidentate (thirteen complexes).

* For Part VI, see M.P. LEITE and J. DE O. CABRAL, *Rev. Port. Quím.*, **20**, 26 (1978).

INTRODUCTION

In all the molecular complexes described in previous papers of this series [1-9], the anionic ligands were simple halide or pseudo-halide ions. These anions are unidentate or ambidentate ligands; as such, they can, at most, behave as bridging ligands.

In the case of oxo anions as ligands and, particularly, in the case of carboxylate ions, such as the acetate ion, other modes of coordination are possible. It is well known that the carboxyl group can be unidentate as well as bidentate, either with a symmetrical or asymmetrical coordination, or even as bridging ligand.

This study was undertaken with the purpose of investigating how the acetate ion would behave in molecular complexes of $Co(II)$ and $Ni(II)$ with monosubstituted pyridine derivatives, as molecular ligands, and how the presence of this bidentate anionic ligand would affect the coordinating ability of these pyridine derivatives.

EXPERIMENTAL

REAGENTS. All reagents were of the purest quality available and were used without further purification. Solvents were dehydrated firstly with anhydrous sodium sulphate and then with Molecular Sieves 4A.

ANALYTICAL PROCEDURES. Conventional EDTA titrations were used for metal analyses [10]. Elemental analyses were carried out in the Department of Chemistry of the University of Manchester Institute of Science and Technology.

PREPARATIONS. All complexes were prepared in anhydrous ethanol by previously-described methods.

PHYSICO-CHEMICAL MEASUREMENTS. Magnetic susceptibilities were measured at $25^\circ C$ by the Gouy method with a Newport variable-temperature Gouy balance system. Mercury(II) tetrakisothiocyanatocobaltate(II) was used as standard, and the diamagnetic corrections were estimated with the use of Pascal's constants.

IR spectra were obtained with a Perkin-Elmer Model 457 recording spectrophotometer, and electronic spectra as Nujol mulls of the solid complexes with a Unicam SP 700C recording spectrophotometer.

Molar conductivities were measured, at $25^\circ C$, on $1,0 \times 10^{-3}$ M methanolic solutions of the complexes

in a Philips PW 9510 cell with a Phillips GM 4249 conductivity bridge.

RESULTS

The analytical data, magnetic moments and colours of the complexes are summarized in Table 1.

In Tables 2 and 3 the spectral data and ligand field parameters for the pseudo-octahedral cobalt(II) and nickel(II) complexes are summarized.

The important IR bands and molar conductivities (in methanol) are recorded in Table 4. The IR spectra of the simple metal acetates were included for comparison purposes.

Table 1
Analytical and magnetic susceptibility data

COMPLEX	COLOUR	FOUND (CALCD) %				μ_{eff} (M.B.)
		M	C	H	N	
$[\text{Co}(\text{CH}_3\text{COO})_2(2\text{-NH}_2\text{py})_2]$	VIOLET	16,20 (16,13)	45,3 (46,0)	4,9 (4,9)	15,4 (15,3)	4,7
$[\text{Co}(\text{CH}_3\text{COO})_2(2\text{-OHpy})_2]$	PINK	16,07 (16,05)	45,9 (45,7)	4,5 (4,4)	7,3 (7,6)	4,9
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-Clpy})_2]$	PINK	14,70 (14,58)	41,8 (41,6)	3,5 (3,5)	6,7 (6,9)	4,8
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-Brpy})_2]$	LIGHT PINK	11,99 (11,95)	34,8 (34,1)	2,5 (2,9)	5,8 (5,7)	4,9
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-OHpy})_2]$	PINK	15,98 (16,05)	45,8 (45,7)	4,3 (4,4)	7,7 (7,6)	4,5
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-NH}_2\text{py})_2]$	BROWNISH RED	16,18 (16,13)	45,7 (46,0)	5,0 (4,9)	15,3 (15,3)	5,3
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-Clpy})_2]$	PINK	14,89 (14,58)	41,7 (41,6)	3,3 (3,5)	6,8 (6,9)	4,9
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-Brpy})_2]$	PINK	12,01 (11,95)	34,6 (34,1)	2,6 (2,9)	5,5 (5,7)	4,8
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-OHpy})_2]$	DARK PINK	16,37 (16,05)	45,6 (45,7)	4,2 (4,4)	7,4 (7,6)	5,2
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-NH}_2\text{py})_2]$	DARK PINK	16,07 (16,13)	45,8 (46,0)	5,0 (4,9)	15,5 (15,3)	4,9
$[\text{Ni}(\text{CH}_3\text{COO})_2(2\text{-NH}_2\text{py})_2]$	GREEN	16,04 (16,08)	46,1 (46,0)	4,9 (4,9)	15,4 (15,3)	3,3
$[\text{Ni}(\text{CH}_3\text{COO})_2(2\text{-OHpy})_2]$	LIGHT GREEN	15,60 (15,99)	45,8 (45,8)	4,3 (4,4)	7,7 (7,6)	3,3
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-Clpy})_2]$	GREEN	14,56 (14,54)	41,8 (41,6)	3,6 (3,5)	6,1 (6,9)	3,3
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-Brpy})_2]$	LIGHT GREEN	11,97 (11,92)	33,8 (34,1)	3,0 (2,9)	5,1 (5,6)	3,2
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-OHpy})_2]$	GREEN	15,98 (15,99)	46,0 (45,8)	4,6 (4,4)	7,1 (7,6)	3,0
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-NH}_2\text{py})_2]$	BLUE	16,11 (16,08)	45,7 (46,0)	4,7 (4,9)	15,1 (15,3)	3,2
$[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-Brpy})_2]$	BLUE	11,64 (11,92)	34,3 (34,1)	2,7 (2,9)	5,6 (5,6)	3,3
$[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-OHpy})_2]$	BLUE	10,97 (10,54)	51,4 (51,7)	4,9 (4,7)	10,2 (10,1)	3,3
$[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-NH}_2\text{py})_2]$	LIGHT GREEN	15,99 (16,08)	45,8 (46,0)	4,3 (4,9)	15,5 (15,3)	3,1

Table 2
Electronic spectral data and ligand field parameters for pseudo-octahedral Co(II) complexes

COMPLEX	λ_1 (cm^{-1})	λ_2 (calcd)	λ_3 (cm^{-1})	$10Dq$ (cm^{-1})	B (cm^{-1})	β
$[\text{Co}(\text{CH}_3\text{COO})_2(2\text{-NH}_2\text{py})_2]$	8235	17555	18765	9320	774	0,801
$[\text{Co}(\text{CH}_3\text{COO})_2(2\text{-OHpy})_2]$	11824	24844	20706	13020	672	0,695
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-Clpy})_2]$	9000	19170	19912	10170	805	0,833
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-Brpy})_2]$	9206	19586	20000	10380	798	0,826
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-OHpy})_2]$	9471	20131	20176	10660	793	0,820
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-NH}_2\text{py})_2]$	9500	20070	18176	10570	650	0,672
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-Clpy})_2]$	9000	24368	20471	12660	656	0,678
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-Brpy})_2]$	8735	18545	18235	9810	705	0,729
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-OHpy})_2]$	8500	18060	18000	9560	704	0,728
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-NH}_2\text{py})_2]$	8529	18149	18647	9620	747	0,775

Table 3
Electronic spectral data and ligand field parameters for pseudo-octahedral Ni(II) complexes

COMPLEX	ν_1 (cm^{-1})	ν_2 (cm^{-1})	$10 Dq$ (cm^{-1})	B (cm^{-1})	β
a)					
$[\text{Ni}(\text{CH}_3\text{COO})_2(2\text{-NH}_2\text{py})_2]$	9412	15235	9412	817	0,785
$[\text{Ni}(\text{CH}_3\text{COO})_2(2\text{-OHpy})_2]$	9000	15000	9000	1000	0,961
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-Clpy})_2]$	9647	15588	9647	825	0,792
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-Brpy})_2]$	10059	16000	10059	774	0,743
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-OHpy})_2]$	9760	15588	9760	786	0,755
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-NH}_2\text{py})_2]$	9588	15647	9588	883	0,849
$[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-Brpy})_2]$	9294	15235	9294	892	0,856
$[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-NH}_2\text{py})_2]$	9882	15706	9882	758	0,728
b)					
$[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-OHpy})_4]$	9471	15059	9471	728	0,699

Table 4
Important ir bands and molar conductances (in methanol)

COMPLEX	$\nu_{\text{ass}}(\text{OCO})$ (cm^{-1})	$\nu_{\text{sym}}(\text{OCO})$ (cm^{-1})	SEPARN. (cm^{-1})	$\delta(\text{OCO})$ (cm^{-1})	CONCN. (mol dm^{-3})	Λ ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	1540	1445	90	675		
$[\text{Co}(\text{CH}_3\text{COO})_2(2\text{-NH}_2\text{py})_2]$	1560	1425	135	680	$1,36 \times 10^{-3}$	39,3
$[\text{Co}(\text{CH}_3\text{COO})_2(2\text{-OHpy})_2]$	1530	1400	130	670	$1,60 \times 10^{-3}$	12,6
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-Clpy})_2]$	1535	1410	125	670	$1,02 \times 10^{-3}$	36,4
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-Brpy})_2]$	1555	1395	160	690	$1,74 \times 10^{-3}$	24,1
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-OHpy})_2]$	1520	1415	105	680	$1,08 \times 10^{-3}$	3,5
$[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-NH}_2\text{py})_2]$	1545	1415	130	670	$0,93 \times 10^{-3}$	49,7
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-Clpy})_2]$	1560	1410	150	680	$0,90 \times 10^{-3}$	26,5
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-Brpy})_2]$	1545	1425	120	660	$0,85 \times 10^{-3}$	25,7
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-OHpy})_2]$	1535	1405	130	670	$0,93 \times 10^{-3}$	38,5
$[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-NH}_2\text{py})_2]$	1540	1410	130	670	$1,07 \times 10^{-3}$	50,2
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	1510	1420	90	680		
$[\text{Ni}(\text{CH}_3\text{COO})_2(2\text{-NH}_2\text{py})_2]$	1540	1435	115	675	$0,96 \times 10^{-3}$	13,9
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-Clpy})_2]$	1525	1410	115	695	$1,02 \times 10^{-3}$	15,8
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-Brpy})_2]$	1530	1380	150	660	$1,44 \times 10^{-3}$	29,1
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-OHpy})_2]$	1575	1420	155	700	$1,38 \times 10^{-3}$	17,3
$[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-NH}_2\text{py})_2]$	1520	1400	120	700	$1,14 \times 10^{-3}$	20,1
$[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-Brpy})_2]$	1550	1400	150	690	$1,09 \times 10^{-3}$	26,8
$[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-NH}_2\text{py})_2]$	1535	1415	120	680	$1,17 \times 10^{-3}$	29,2
$[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-OHpy})_4]$	1560	1385	175	660	$1,01 \times 10^{-3}$	35,2

DISCUSSION

In all the nineteen complexes herein reported the metal ion is six-coordinated by the ligands. Since

the pyridine derivatives are unidentate, attention will be focused on the coordination behaviour of the acetate ion.

The analytical results support the proposed formulation of the complexes. With the exception of $[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-OHpy})_4]$, which has a 1:2:4 stoichiometry, all the complexes have stoichiometries corresponding to 1:2:2. The colours and magnetic moments of the complexes are consistent with six-coordination of the metal ions.

The molar conductivities in methanol are well below the range accepted for 1:1 electrolytes [11,12]. Thus, although there are clear signs of dissociation, it is safe to assume that the complexes are molecular and monomeric.

The absence of any bands with frequencies above 1600 cm^{-1} , assignable to $\nu_{\text{ass}}(\text{OCO})$ in symmetrical bridging acetate groups, precludes this mode of coordination [13,14]. It seems, therefore, that in these complexes the other three modes of coordination of the acetate ion can be found.

UNIDENTATE COORDINATION

Only in the case of $[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-OHpy})_4]$ were found bands at 1560 cm^{-1} , assignable to $\nu_{\text{ass}}(\text{OCO})$, and at 1385 cm^{-1} , due to $\nu_{\text{sym}}(\text{OCO})$, with a separation of 175 cm^{-1} , as expected for unidentate coordination. Thus, this complex can be formulated as shown in fig. 1 in agreement with its chemical and physical properties. This behaviour contrasts with the other complex of 4-hydroxypyridine, $[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-OHpy})_2]$, to be discussed below. The explanation can possibly be found in the greater tendency of Ni(II) for hexacoordination with unidentate ligands.

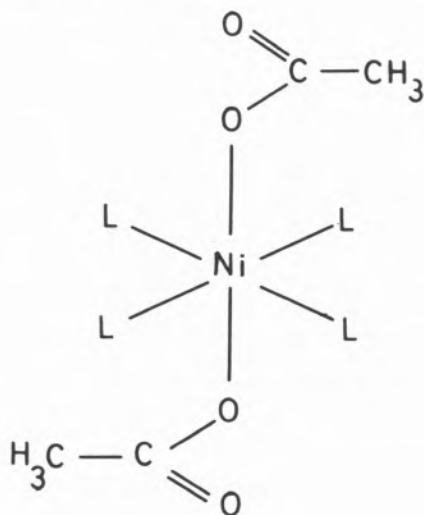


Fig. 1

ASYMMETRICAL BIDENTATE COORDINATION

This unusual coordination mode could be detected in the following four complexes: $[\text{Co}(\text{CH}_3\text{COO})_2(3\text{-Brpy})_2]$, $[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-Clpy})_2]$, $[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-OHpy})_2]$ and $[\text{Ni}(\text{CH}_3\text{COO})_2(4\text{-Brpy})_2]$. The carboxy-band frequencies are at $1550\text{--}1575\text{ cm}^{-1}$ and $1395\text{--}1420\text{ cm}^{-1}$ (separations $150\text{--}160\text{ cm}^{-1}$), so suggesting asymmetrical bidentate coordination of the acetate ion [13,14,15]. The complexes can be depicted as in fig. 2 to show two

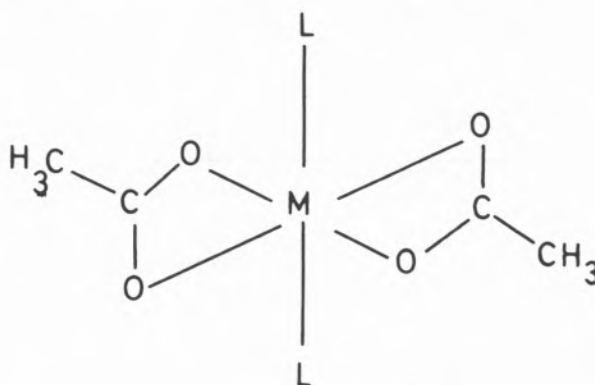


Fig. 2

equal short, and two equal long, O — M bonds. The case of $[\text{Ni}(\text{CH}_3\text{COO})_2(3\text{-Brpy})_2]$ is more doubtful: although the band separation is 150 cm^{-1} , the carboxy-bands are at 1530 cm^{-1} and 1380 cm^{-1} , frequencies significantly lower than for the other four complexes.

Taking into account the band separation, asymmetrical bidentate coordination is tentatively assigned to this complex.

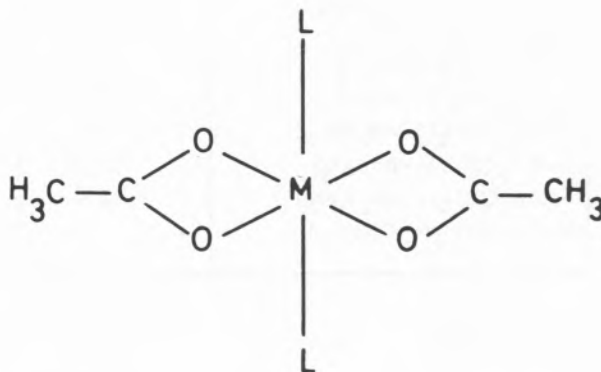


Fig. 3

SYMMETRICAL BIDENTATE COORDINATION

By the infra-red criterion all the other thirteen complexes belong to this type of acetate coordination. Their formulae can be represented by showing four equal, medium-length O — M bonds. This formulation is also consistent with their chemical and physical properties (fig. 3).

SYMMETRICAL VS. ASYMMETRICAL BIDENTATE COORDINATION

From the available data in this work it is difficult to discern what experimental factors will favour one or the other mode of acetate coordination.

For six-coordination the effective ionic radii generally accepted for Co^{2+} and Ni^{2+} are 0.74 Å (high spin) and 0.70 Å, respectively. The values are so close that no significant difference is to be expected in steric constraints for these two metal ions as far as their effective sizes are concerned.

Different lengths have been reported for the O — M bonds: two equal shorter bonds in asymmetrical bidentate complexes, four equal medium-length bonds in symmetrical, and two equal longer bonds in asymmetrical bidentate complexes [13].

If these facts are of any importance, the position and bulkiness of the substituents in the pyridine ring would be paramount in favouring one mode over the other mode of acetate coordination: possibly bulky substituents in the 2 position would favour symmetrical coordination, owing to the shorter O — M bond in the asymmetrical case, and this effect would become successively less pronounced as the substituent is moved to the 3 and 4 positions. The experimental data obtained in the present work do not confirm or negate this hypothesis.

Unfortunately all attempts at preparing complexes with 2-chloro- and 2-bromopyridine failed. This failure may be a consequence of steric hindrance from the bulkiness of the substituents. The preparation was successful with 2-amino- and 2-hydroxypyridine and in all four complexes with these molecular ligands a symmetrical bidentate acetate coordination was detected. Whether these facts relate to a smaller size of the substituent in the 2 position or to the predominance of a tautomeric form of the ligands is a question that remains unanswered.

Comparing the two complexes with 3-hydroxypyridine no reason can be given to explain the difference between the Co(II) and the Ni(II) complexes. The same can be said about the two complexes with 4-bromopyridine. In any case it is interesting to notice that asymmetric coordination appears in the Ni(II) complexes and symmetric in the Co(II) complexes but this leads nowhere because a substituent in the 4 position is expected to give the least possible steric hindrance.

The complexes which could be prepared with other substituents in the 4 position (4-hydroxy- and 4-aminopyridine) belong to the symmetrical mode of coordination. To this same mode belong the two complexes with 3-chloropyridine, and the two with 3-aminopyridine.

Since the Ni(II) complex with 4-chloropyridine could not be prepared, no comparison is possible with $[\text{Co}(\text{CH}_3\text{COO})_2(4\text{-Clpy})_2]$.

Both complexes with 3-bromopyridine seem to have asymmetrical bidentate coordination of the acetate ion in contrast with the corresponding complex with 3-chloropyridine. Whether this results from the difference in size between Br and Cl cannot be asserted with any reasonable degree of certainty.

It is vaguely possible that if the missing links in this series of complexes could be prepared, as well as some series of complexes with other pyridine derivatives, a pattern could be found for the symmetrical vs. asymmetrical bidentate coordination behaviour of the acetate ion.

Efforts are being made in this direction and will be reported in due course of time.

ACKNOWLEDGEMENT

The unfailing encouragement, help, and advice of Prof. J de O. Cabral is gratefully acknowledged, as well as the willingness of Dr. R. Perry (UMIST) in undertaking the elemental analyses. This work was carried out with the support of INIC, Lisbon (CIQ, QP/1, Linha 3).

REFERENCES

- [1] J. DE O. CABRAL, *Anais Fac. Ciênc. Porto*, **47**, 25 (1964).
- [2] J. DE O. CABRAL, M.T. MONTEIRO, *Rev. Port. Quím.*, **10**, 56 (1968).
- [3] J. DE O. CABRAL, M.F. CABRAL, *Rev. Port. Quím.*, **12**, 85 (1970).
- [4] J. DE O. CABRAL, M.T. LEITE, M.F. CABRAL, *Proceedings of The XVI International Conference on Coordination Chemistry, Dublin, Ireland, R34* (1974).
- [5] M.T.P. LEITE, *Rev. Port. Quím.*, **16**, 21 (1974).

- [6] M.T.P. LEITE, J. DE O. CABRAL, *Rev. Port. Quím.*, **20**, 26 (1978).
- [7] J. DE O. CABRAL, M.F. CABRAL, M.T.P. LEITE, Proceedings of the XVIII International Conference on Coordination Chemistry, São Paulo, Brasil, 165 (1977).
- [8] J. DE O. CABRAL, M.T.P. LEITE, Proceedings of the XXI International Conference on Coordination Chemistry, Toulouse, France, 469 (1980).
- [9] M.T.P. LEITE, 5.º Encontro Anual da Soc. Port. Quím., Porto, C30.19 (1982).
- [10] H.A. FLASCHKA, "EDTA Titrations", Pergamon Press, 1959.
- [11] W.J. GEARY, *Coord. Chem. Rev.*, **7**, 81 (1971).
- [12] STEPHEN H. WHEELER, STEVEN C. ZINGHEIM, LAWRENCE C. NATHAE, *J. inorg. nucl. Chem.*, **40**, 779 (1978).
- [13] N.F. CURTIS, *J. Chem. Soc. (A)*, 1579 (1968).
- [14] G. COLOMBINI, C. PRETI, *J. inorg. nucl. Chem.*, **37**, 1159 (1975).
- [15] M. VIDALI, P.A. VIGATO, U. CASELLATO, *J. inorg. nucl. Chem.*, **37**, 955 (1975).