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X-Ray Photoelectron and Potentiometric Studies of Some Calcium Complexes

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Abstract

ESCA core line spectra was obtained for citrate, dipicolinate and tripolyphosphate salts. The mode of coordination of these species with calcium ions was assessed from the changes in the binding energies of the different core levels, as well as from the changes in the profiles of their spectral envelopes. The formation constants of both normal and protonated chelates of these anions with calcium and magnesium ions were determined at 30 °C. The free energy changes for these species are discussed in terms of the electrostatic model and correlated with the effective anionic charges of the different ligands.

Introduction

In previous papers the mode of ligand coordination and bonding of various phosphate [1] and silicate [2] species with calcium and magnesium ions was discussed. Among other non-phosphate potential sequestering agents for calcium ions are the citrates and dipicolinates, as well as various polyaminocarboxylates. Recently, Cheng *et al.* [3] and Yoshida *et al.* [4, 5] reported a detailed XPS study of EDTA and its complexes with various measured divalent metal ions. Measurements on the dipicolinate complexes are limited to the lanthanide, cobalt(II) and silver(II) species [6]. Related photoelectron spectroscopic studies of a variety of other pyridinecarboxylate complexes have also been reported [6, 7].

In order to improve our understanding of the coordination chemistry of these species, the solid complexes of the calcium ion have been synthesized and characterised by IR and XPS, as well as the equilibrium constants in solution (evaluated potentiometrically).

Experimental

Materials

Commercial grade sodium tripolyphosphate (STP) was purified by recrystallisation four times from methanol–water mixtures [8]. The purity of the final product ($Na_5P_3O_{10}\cdot 6H_2O$) was checked by elemental analyses. Dipicolinic and citric acids and their sodium salts were purchased as analytical grade reagents and used as such. The calcium salts were prepared in the laboratory and analysed for the constituent elements.

Procedures

Potentiometric measurements

A suitable aliquot of the ligand solution was titrated potentiometrically in the absence and in the presence of the metal ion. The pH was recorded using a Radiometer model pH M 84 fitted with a combined glass–calomel electrode. The titration cell was thermostatted to 30 °C with constant-temperature water circulated through a sealed jacketed cell. Purified nitrogen gas was passed through the solution during the measurements. The ionic strength of the reacting solutions was kept constant at 0.10 *M* using NaCl as a background electrolyte. To convert the hydrogen ion activity into the concentration, the value of 0.782 was used as the activity coefficient.

X-Ray photoelectron spectroscopic measurements

The XPS measurements were recorded on a V.G. ESCA-3 spectrometer at the liquid nitrogen temperature and under a vacuum of about 10^{-7} Torr. Al K_α (1486.6 eV) X-ray radiation was used as the excitation source. Samples were ground and dusted onto a double-sided adhesive tape. The binding energies, E_B, of the C(1s), N(1s), O(1s) and P(2p) electrons were derived by means of the familiar relationship, $E_B = h\nu - E_{kin}$, where $h\nu$ is the photon energy and E_{kin} is the measured photoelectron energy. For calibration purposes a thin layer of gold was evaporated onto the surface of the sample and the values of the binding energies were measured with reference to the gold $4f_{7/2}$ peak (84.0 eV).

IR measurements

IR spectra were obtained with a Pye-Unicam SP3-200 IR spectrometer using KBr discs.

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TABLE I. Core Electron Binding Energies for the Different Citrate, Dipicolinate and Tripolyphosphate Species.

Compound	Level	E_B (eV)	Assignment	Height
Citric acid	O 1s	532.7	O_1	38.7 ± 0.1
		531.4	O_2	
	C 1s	288.3	C_1	15.4 ± 0.1
		285.0	C_2	
		283.1	C_3	
Sodium citrate	O 1s	533.7	O_3	32.5 ± 0.2
		531.4	O_1, O_2	
	C 1s	288.2	C_1	13.3 ± 0.1
		285.9		
		284.8	C_2	
		283.7	C_3	
Calcium citrate	O 1s	531.6	O_1, O_2	52.0 ± 0.1
	C 1s	288.4	C_1	21.0 ± 0.2
		285.8	C_2	
		284.5	C_3	
Dipicolinic acid	O 1s	533.7	O_1	9.1 ± 0.1
		531.8	O_2	
	C 1s	289.0	C_1	8.5 ± 0.2
		285.0	C_2–C_4	
	N 1s	399.2		1.7 ± 0.1
Sodium dipicolinate	O 1s	531.2	O_1, O_2	13.8 ± 0.1
	C 1s	288.1	C_1	11.0 ± 0.1
		285.3	C_2–C_4	
	N 1s	399.3		2.35 ± 0.1
Calcium dipicolinate	O 1s	531.7	O_1	17.4 ± 0.1
		530.1	O_2	
	C 1s	287.3	C_1	13.6 ± 0.1
		284.5	C_2–C_4	
	N 1s	398.7		2.9 ± 0.1
Sodium tripolyphosphate	O 1s	531.9		49.0 ± 0.2
	P 2p	134.4		7.9 ± 0.1
Calcium tripolyphosphate	O 1s	533.0		52.5 ± 0.1
		531.1		
	P 2p	135.4	bridging P_1	8.1 ± 0.1
		133.9	terminal P_2	

Results and Discussion

Table I lists the binding energies for the compounds studied. The accuracy of these measurements was assessed by repeated measurements of the core levels and the deviation was found to be ~0.20 eV for the C(1s) and O(1s) spectra and ~0.10 eV for the N(1s) and P(2p) spectra. The high uncertainty in the former case is a consequence of the great number of peaks under the C(1s) and O(1s) spectral envelopes.

The C(1s) spectra of all the dipicolinate and citrate species show the presence of two distinguished peaks, the separation energy of which is a function of the counter ion ($H^+ > Na^+ \cong Ca^{2+}$). The profiles of these spectra are shown in Fig. 1(A) and (B) respectively. The high energy peak is assigned to the carboxylate C(1s) binding energy whereas the peak on the lower energy side is assigned to the backbone carbons. In the case of dipicolinic acid the two peaks are almost separated. The full width half heights (FWHH) of

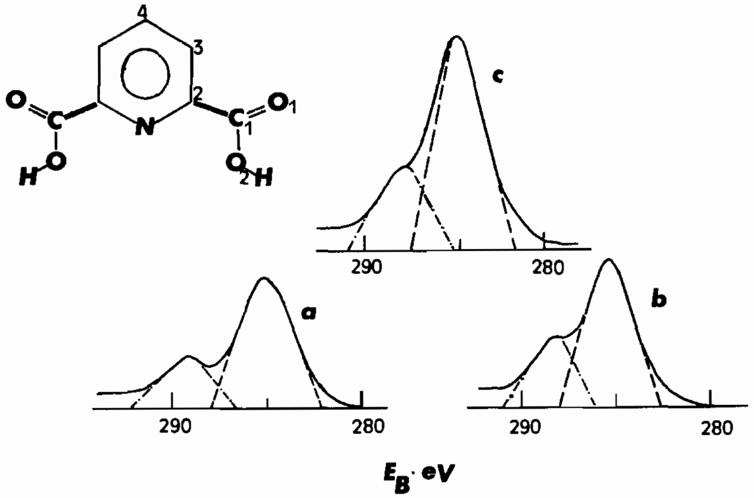

Fig. 1A. Carbon (1s) spectra for dipicolinate species. a) The acid; b) sodium salt; c) calcium complex.

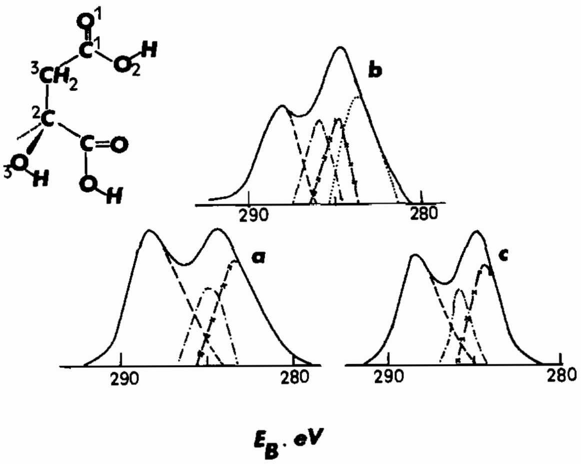

Fig. 1B. Carbon (1s) spectra for citrate species. a) The acid; b) sodium salt; c) calcium complex.

these peaks were taken as guiding values to deconvolute the other related envelopes to give peak areas proportional to those required by the molecular formula. The same method was used to analyse the citrate spectra.

Apart from the satellite observed for the oxygen (1s) spectra of the sodium salts, only one peak is obtained in all cases. In the case of anhydrous dipicolinates, the broadening of the O(1s) peak of the acid and calcium salts relative to that of the disodium salt probably accounts for the presence of the two carboxylate oxygens in non-equivalent potential environments. Similar arguments may be used to explain the broadening observed in the oxygen spectra of the citrate and phosphate species. Although hydrated citrate and phosphate samples were used in these measurements, integration of peak area and

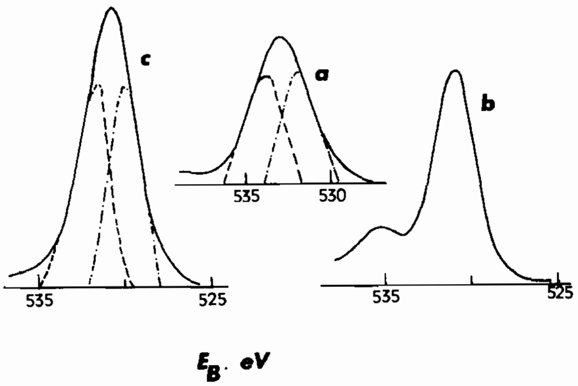

Fig. 2. Oxygen (1s) spectra for a) dipicolinic acid, b) sodium dipicolinate and c) calcium dipicolinate.

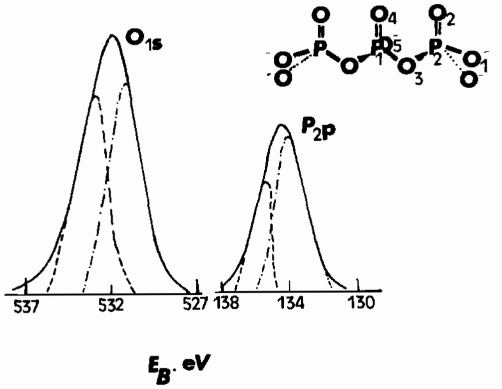

Fig. 3. Phosphorus (2p) and oxygen (1s) spectra of calcium tripolyphosphate.

subsequent analyses for the elemental constituents showed however that the water of hydration is lost during the spectral measurements. A sample of the deconvoluted peaks is illustrated in Fig. 2.

TABLE II. Calculated Fractional Charges of the Different Species.

A) Citrates

Species	O_1	O_2	O_3	C_1	C_2	C_3
Acid	−0.28	−0.42	−0.44	0.40	0.15	−0.06
Sodium salt	−0.54	−0.54	−0.44	0.35	0.15	−0.06
Sodium salt[a]	−0.54	−0.35	−0.32	0.35 0.37	0.16	−0.06
Calcium cpx[b]	−0.51	−0.51	−0.94	0.36	0.10	−0.06
Calcium cpx	−0.52	−0.52	−0.44	0.35	0.15	−0.06

B) Dipicolinates

	O_1	O_2	N	C_1	C_2	C_3	C_4
Acid	−0.28	−0.42	−0.14	0.40	0.07	−0.04	−0.03
Sodium salt	−0.54	−0.54	−0.14	0.35	0.07	−0.04	−0.03
Calcium cpx	−0.28	−0.75	−0.14	0.37	0.07	−0.04	−0.03
Calcium cpx[c]	−0.28	−0.74	−0.54	0.37	0.04	−0.04	−0.03

C) Tripolyphosphates

	O_1,O_5	O_2,O_3,O_4	P1	P_2
Sodium salt	−0.86	−0.43	1.02	0.98
Calcium cpx	−0.80	−0.43	1.02	0.99

[a] Assuming intramolecular hydrogen bonding between the OH group and the adjacent carboxylate group. [b] Based on structures where the OH group is coordinated to the metal ion. [c] Based on structures where the pyridine ring nitrogen is coordinated to the metal ion.

The phosphorus (2p) spectra of the sodium as well as that of the calcium tripolyphosphates showed a symmetrical peak with a FWHH of 3.10 eV compared to 1.85 eV reported for the orthophosphate [1]. Two peaks indicated by broken lines in Fig. 3 have been assigned to the bridging (P_1) and terminal (P_2) phosphorus atoms respectively.

Effect of Coordination on the Binding Energy of the Ligand Donor Atoms

Comparison of the E_B values of the different levels of the sodium and calcium dipicolinates showed a significant lowering in the N(1s) and O_2(1s) binding energies, which indicates binding of both sites to the calcium ion. This is consistent with the findings of Yoshida [7] for the monopicolinate species. On the other hand, the lack of high resolution of the ESCA technique rendered it very difficult to speculate on the participation of the citrate hydroxyl group in coordinating the metal ion. However, the C(1s) spectral envelopes for the sodium salt displayed a marked change in symmetry as shown in Fig. 1B. Deconvolution of this peak suggests a splitting in the peak assigned to the carboxylate carbons into two peaks of relative intensity 2:1. Such changes in electronic density could be induced through a strong intramolecular hydrogen bonding of the OH group with one of the COO^- groups. The developments of new bands in the IR spectra of the sodium citrate at 3260 cm^{-1} (m, broad), 2960 cm^{-1} (w) and 2920 cm^{-1} (w) is consistent with a strong intramolecular association within the molecule. Kuroda and Mason [9] showed from their X-ray structural analyses of the structurally related sodium ammonium tartrate crystal that the carboxylate group planes are so disposed that one of the constituent oxygen atoms and the adjacent hydroxyl group bonded to the α-carbon atom form an intramolecular hydrogen bond.

The ESCA spectra of both sodium and calcium tripolyphosphates are similar, except for the changes anticipated in the E_B values of the O(1s) and P(2p) levels as a result of varying the positive potentials of the counter ions. The IR spectra on the other hand show a considerable shift in the sym. and asym. modes of vibration of the PO_3^{2-} group, located at *ca.* 962 and 1080 cm^{-1} and 1000 and 1105 cm^{-1} for the sodium and calcium salts respectively.

Charge-potential Model

In the electrostatic potential model, core electron binding energies E_B for a molecular solid are related to the molecular charge distribution by

$$E_B = E_B^\circ + kq_i + \sum_{j \neq i} q_j/R_{ij} \qquad (1)$$

where E_B° is a reference level, q_i is the charge on atom i, q_j is the charge on atom j displaced by a distance R_{ij} from i, and k is a constant. The determination of molecular charge distribution of the different com-

TABLE III. Potentiometric Titration Data of Calcium-Dipicolinate System[a] (T = 298 K, I = 0.10 M (NaCl)).

Vol. of Titrant ml	pH	$[L^{2-}] \times 10^5$ M	$\bar{n}$
1.00	2.602	2.703	0.534
1.60	2.799	4.106	0.633
1.80	2.885	4.903	0.673
1.90	2.933	5.401	0.697
2.00	2.986	6.010	0.721
2.10	3.045	6.767	0.747
2.20	3.108	7.647	0.777
2.30	3.178	8.748	0.810
2.40	3.257	10.171	0.844
2.50	3.348	12.098	0.881
2.60	3.454	14.798	0.918
2.70	3.576	18.596	0.958
2.80	3.716	24.051	0.999
2.90	3.852	30.168	1.049
3.00	4.016	39.754	1.090
3.10	4.180	51.088	1.132
3.20	4.343	63.614	1.174
3.30	4.516	78.146	1.211
3.42	4.716	91.244	1.277

[a] Cup contents: $[Ca(II)]_i = 2.5 \times 10^{-3}$ M; $[Dipic]_i = 5 \times 10^{-3}$ M; pH_i = 2.376; Vol_i = 75 ml. The subscript i refers to initial and $[L^{2-}]$ denotes the free ligand concentration. Titrant is 0.200 M NaOH.

TABLE IV. Protonation Constants and Stability Constants for Some Magnesium and Calcium Complexes $M_qH_jA_p$ at 298 K and I = 0.10 M (NaCl).

Ligand	$q\ j\ p$	Species	Log β_{qjp}
Dipicolinate	0 1 1	HL^-	4.56 ± 0.02
	0 2 1	H_2L	6.21 ± 0.06
	1 0 1	MgL	1.94 ± 0.03
	1 0 1	CaL	4.59 ± 0.03
	1 0 2	CaL_2^{2-}	7.28 ± 0.07
Citrate	0 1 1	HL^{2-}	5.48 ± 0.02
	0 2 1	H_2L^-	9.79 ± 0.04
	0 3 1	H_3L	12.81 ± 0.14
	1 0 1	MgL^-	3.46 ± 0.06
	1 1 1	MgHL	7.61 ± 0.10
	1 0 1	CaL^-	3.43 ± 0.04
	1 1 1	CaHL	8.28 ± 0.20
Triphosphate	0 1 1	HL^{4-}	7.70 ± 0.02
	0 2 1	H_2L^{3-}	13.11 ± 0.05
	0 3 1	H_3L^{2-}	15.88 ± 0.20
	1 0 1	MgL^{3-}	5.82 ± 0.06
	1 1 1	$MgHL^{2-}$	11.57 ± 0.10
	1 0 1	CaL^{3-}	4.90 ± 0.10
	1 1 1	$CaHL^{2-}$	10.85 ± 0.15

pounds was obtained by means of a FORTRAN IV CDC program (the details are given in the Appendix). The values of calculated q's are summarised in Table II. These charges were used with the experimental binding energies and suggested molecular geometries to yield values for E_B° and k for the different core levels using eqn. 1. Thus for the O(1s) level the values obtained from the least squares analyses are 532.2 ± 0.2 eV and 8.9 ± 0.3 as the intercept and slope respectively. The corresponding data for the C(1s) level of the carboxylate groups were found to be 279.5 ± 0.3 eV and 24.8 for E_B° and k respectively. The slopes observed in both cases are in accord with the results of studies on a variety of solids which yielded values closely grouped around 9.5 and 23.5 for the oxygen and carbon levels respectively. The observed intercepts differ from reported values by almost 5–5.5 eV. This difference may be attributed to intermolecular potential effects in addition to the intramolecular ($\Sigma_{j \neq i} q_j/R_{ij}$) potential term.

The fractional charges calculated and listed in Table II were checked against those calculated from equilibrium constant data through the Münze equation [11]. The β_{qjp} values were calculated from potentiometric measurements following standard procedures [12]. A sample set of the potentiometric data for the calcium dipicolinate system is provided in Table III, whereas Table IV reports all the constants obtained for the studied systems. These constants are in good agreement with those reported previously under comparable experimental conditions [13].

Assuming the dominance of electrostatic interactions within these species, then the observed values of log β_{qjp} would be expected to vary linearly with the effective anionic charge, Z_a'. Accordingly,

$$\Delta G = \frac{Ne^2 Z_c Z_a'}{418.7 D_{eff} d} - RT\nu \ln 55.51 + RT\Sigma \ln f_{(\mu)} \qquad (2)$$

where N is Avogadro's number, e is the unit charge, D_{eff} is the effective dielectric constant, d is the distance between the charged centers, ν is the change in the number of reacting species and

$$\Sigma \ln f_{(\mu)} = -\left((\Delta Z^2)\cdot\frac{0.511(\mu)^{1/2}}{1 + Ba^\circ(\mu)^{1/2}} - C(\mu)^{1/2} - E\right) \qquad (3)$$

($B = 0.33$, $C = 0.75$, $E = -0.15$, $a^\circ = 4.3$ and $\Delta Z^2 = (Z_c + Z_a')^2 - (Z_c)^2 - (Z_a')^2$).

Recently, Choppin and Orebaugh [14] have used this equation successfully to interpret their results of fluoride, squarate, croconate, kojate, maltotate and tropolonate complexes with lanthanide and actinide ions. In their treatment they allowed D_{eff} to be a parameter which varies with the cationic charge

TABLE V. Estimated Anionic Charges and Calculated Free Energy Changes for the Different Metal–Ligand Systems Using Münze's Equation.

Ligand	Metal Ion	Species	$-\Delta G_{\mathrm{expt}}$ kcal/mol	$-\Delta G_{\mathrm{calc.}}$ kcal/mol	D_{eff}	d^{a} Å	$-Z_{\mathrm{a}}'$ (calc.)
Citrate	Ca	CaL	4.67	4.67	45.7	3.41	1.85
		CaHL	3.81	3.82	49.0	3.41	1.75
	Mg	MgL	4.71	4.69	48.8	3.05	1.76
		MgHL	2.90	2.89	56.7	3.05	1.54
Dipicolinate	Ca	CaL	6.24	6.21	50.0	2.45	1.73
	Mg	MgL	2.64	2.63	65.7	2.41	1.32
Tripolyphosphate	Ca	CaL	6.67	6.67	38.5	3.55	2.06
		CaHL	4.29	4.31	45.8	3.55	1.84
	Mg	MgL	7.92	7.89	39.0	3.10	2.05
		MgHL	5.27	5.26	46.3	3.10	1.83
Succinate[b]	Ca	CaL	1.63	1.62	60.9	3.41	1.43
Maleate[b]	Ca	CaL	3.30	3.32	54.6	3.41	1.60
Phthalate[b]	Ca	CaL	3.31	3.32	54.6	3.41	1.60

[a] Estimated values from reported bond distances [15] [b] Values of $\Delta G_{\mathrm{expt.}}$ were taken from reference [13].

Z_c at fixed Z_a'. Best fit was obtained with $D_{\mathrm{eff}} = 79.8$ for $\mathrm{M^{+2}L^{-1}}$, 57.0 for $\mathrm{M^{+3}L^{-1}}$ and 40.8 for $\mathrm{M^{+4}L^{-1}}$ systems. In fact these values are inversely proportional to the product $(Z_cZ_a')^{1/2}$. In the present calculations the value of the effective anionic charge Z_a' was taken as a parameter whereas the corresponding D_{eff} values were extrapolated from the D_{eff} *vs.* $(Z_cZ_a')^{1/2}$ relationship. In all calculations iteration continued, to minimise the difference $(\Delta G_{\mathrm{expt}} - \Delta G_{\mathrm{calc.}})$. A summary of the results obtained is given in Table V.

Although the errors in Z_a' values reflect other errors in the measured ΔG_{expt} and the estimated d and D_{eff} values, these values could be used in a qualitative sense to give an insight into the mode of coordination of these ligands.

The effective charge calculated for a typical saturated dicarboxylate ligand (succinate) is significantly lower than that calculated for the normal citrate complex and its monoprotonated species. This extra charge felt by the metal ion cannot be rationalised, except by assuming structures where the metal ion is coordinated to the α-hydroxy group. Similarly, if the assumption is made that the tripolyphosphate moiety acts as a tridentate ligand using two terminal oxygens and the third attached to the bridging phosphorus [16], then the metal ion is expected to feel a total anionic charge of −1.97 units (estimated from the charges calculated for $\mathrm{Ca_5(P_3O_{10})_2}$ as shown in Table II and considering delocalisation of charge between equivalent atoms). This value compared well with that calculated based on Münze's equation (−2.06 units). This agreement indicates that there has been no major perturbation of the charge distribution between solution and solid species.

The extra stability gained by the dipicolinate systems over aromatic *ortho*-dicarboxylates (*e.g.* phthalates) and unsaturated *cis*-dicarboxylate (maleate) ligands is a little peculiar, particularly if the distance separating the two carboxylate groups is taken as a limiting factor. This distance is estimated to be 2.40 Å for the dipicolinate ligand which accounts for the ligand high sensitivity toward the metal ion size for both magnesium and calcium ion chelates. Also, it rationalises the large decrease in ΔG value for MgL species compared to that of the CaL complex. Similar conclusions were also inferred from measurements involving lanthanide ion probes [17].

Appendix

The net charge q_A, on an atom A may be calculated according to the relationship,

$$q_A = Q_A + \sum_{A \neq B} nI_{AB}$$

where Q_A is the formal charge on the atom A, n is the bond order and the summation term of the partial ionic character I_{AB}, is over all the bonds to atom A. According to Pauling [18], the partial ionic character, I_{AB}, of the bond A–B is given by

$$I_{AB} = 1 - \exp[-\tfrac{1}{4}(\chi_A - \chi_B)^2]$$

where χ_A and χ_B are the electronegativities of the atoms A and B respectively. The sign of the electronegativity difference of the elements involved in the bond determines the sign of I.

TABLE VI. Calculated Charges, PMR[a] Shift Data and N(1s) Binding Energy[b] Data for some Metal–EDTA Complexes.

No.	Species	q_N	q_O (Av.)	q_{COO}	δ_α[c] ppm	δ_β[c] ppm	N(1s) B.E. eV
1	Na_2MgY	−0.396	−0.588	−0.840	3.20	2.67	399.3
2	Na_2CaY	−0.487	−0.635	−0.945	3.14	2.55	399.2
3	Na_2BaY	−0.512	−0.647	−0.973	3.09	2.48	399.1
4	NaLaY	−0.455	−0.544	−0.743	3.38	2.79	
5	NaLuY	−0.354	−0.488	−0.620	3.46	2.85	
6	NaYY	−0.401	−0.515	−0.678	3.44	2.83	
7	Na_2PBY	−0.325	−0.547	−0.749	3.55	3.15	399.6
8	Na_2MnY	−0.290	−0.525	−0.701			399.3
9	Na_4Y	−0.151	−0.538	−0.730	3.01	2.47	399.2

[a] Data were extrapolated from references [19–21]. [b] Data obtained from reference [5]. [c] α = acetate protons; β = ethylenic protons; shifts are relative to DSS.

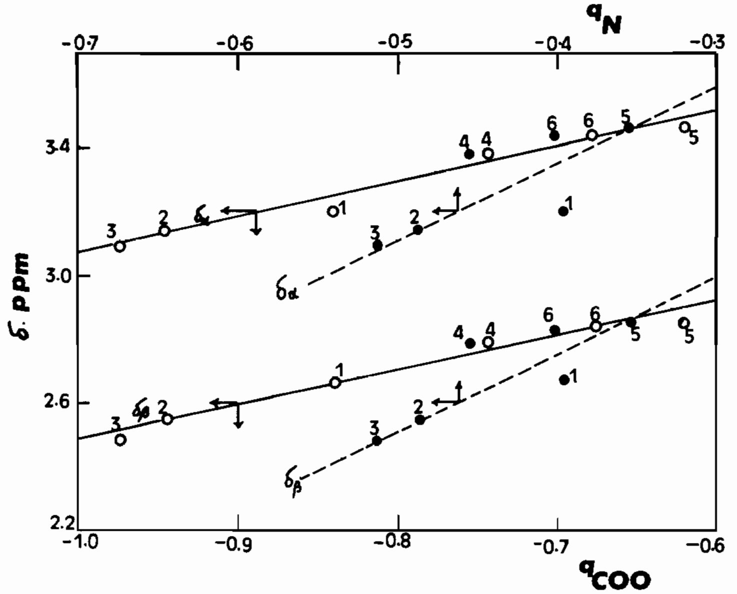

Fig. 4. Correlations of the PMR chemical shift data of the acetate (δ_α) and ethylenic (δ_β) protons of some EDTA complexes as a function of the fractional charges calculated on nitrogen atoms (q_N) and carboxylate groups (q_{COO}).

This method of calculation has been extensively used to correlate the values of q_A with the binding energies of the electrons of the atom A. This method proved to be successful when the values of I_{AB} are quite different from one species to the other, *i.e.* when at least one of the atoms connected to A is different from one molecule to the next in the series. However, in many cases, *e.g.* different MP species (M = Ca^{2+}, Mg^{2+}, Na^+ or K^+ and P = *ortho-*, pyro- or tripolyphosphate), the charge in the phosphorus electron binding energies [1], which is presumably due to changes in the fractional charge on the central phosphorus atom upon changing the counter metal ion or with increasing the chain length of the condensed phosphate groups, does not necessarily meet this requirement. In each case the phosphorus atom is tetrahedrally surrounded by four oxygen atoms. For these particular systems an iterative way of charge calculation has been suggested. After the first calculation cycle the value of χ for each atom in the molecule is simply corrected for the charge by assuming that one formal charge changes the electronegativity value of this particular element by approximately two thirds of the electronegativity difference between that element and the next in the periodic table. In this way a feedback of the charge of the counter ions will be reflected on that of the central atoms. The iteration process is continued for a number of cycles so as to minimise Δq_A (the difference of the calculated charges between two successive iterations) to less than 0.001 units.

These calculations are straightforward for simple diatomic or triatomic molecules. For polyatomic molecules however this method has proved to be time consuming. The proposed CDC* program follows essentially the same steps. The program is written in FORTRAN IV and is capable of calculating fractional charges in any molecule, regardless of its geometry and bond order.

To test the performance of this program the charge distributions on some EDTA–metal complexes were calculated. The values of q_X (X being the coordinated nitrogen, oxygen or the overall charge on a coordinated carboxylate group) are listed in Table VI. In this treatment hexa-coordination is assumed, with the counter sodium ions equivalently located between carboxylate groups. Initial formal charges were taken as zero. At the end of iterations hard metal ions assumed the expected formal charges, whereas the charges calculated on soft metal ions were partially compensated to an extent proportional to the difference $\Delta\chi$ for the metal–donor atom bond. Plots for q_{COO} (or q_N) as a function of the chemical shift δ for both the acetate protons and ethylenic protons [19–21] gave the previously-observed correlation of the dependency of the chemical shift on the effective metal charge density for these complexes [19] (see Fig. 4).

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*A listing of the program together with input data formats will be supplied upon request.