Studies on Metal Carboxylates. Part III.[1] Pyridine-2,6-dicarboxylates of the Lanthanides. Synthesis and Spectral Studies and the *X*-ray Photoelectron Spectra of Several Pyridine Carboxylate Complexes

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The lanthanide(III) acetates react with aqueous solutions of pyridine-2,6-dicarboxylic acid (dipicolinic acid, $dpcH_2$) to afford two series of complexes, $Ln(dpc)(dpcH),6H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Gd, and Tb) and $Ln(dpcH)_3,H_2O$ (Ln = Sm, Gd, Tb, Dy, Ho, or Yb). The samarium complex $Sm(dpc)(dpcH),6H_2O$ was isolated in α- and β-forms. *X*-Ray powder data show that within each series the complexes are isostructural. The electronic absorption spectra of the complexes have also been recorded. The *X*-ray photoelectron spectra of the dehydrated species Ln(dpc)(dpcH) (Ln = Ce or Pr) and $Dy(dpcH)_3$ have been investigated and the C(1*s*), N(1*s*), and O(1*s*) binding energies measured. Attempts to determine the Ce, Pr, and Dy 4*s* binding energies were unsuccessful. Related measurements of the C(1*s*), N(1*s*), and O(1*s*) binding energies of several pyridine carboxylates of manganese(II), cobalt(II), nickel(II), and silver(II) are also described.

PYRIDINE-2,6-DICARBOXYLIC ACID (dipicolinic acid) can co-ordinate as a neutral ($dpcH_2$), monoanionic (dpcH), or dianionic (dpc) terdentate donor. Our interest in this molecule arose from its stabilization of the silver(II) oxidation state to form a complex which can be formulated as $Ag(dpc)(dpcH_2),xH_2O$ (x = 1 or 4).[2-4] Subsequently, we found [5] that its complex with nickel(II), bis(pyridine-2,6-dicarboxylato)nickel(II) trihydrate, is best represented as $Ni(dpcH)_2,3H_2O$. The versatile bonding characteristics of this ligand prompted us to investigate its metal complexes in some detail and in the present report we describe our studies on several of the lanthanide(III) derivatives.

EXPERIMENTAL

The hydrated lanthanide acetates, of general formula $Ln(OAc)_3,xH_2O$, were obtained from Apache Chemicals, Inc., Illinois or Bradford Scientific, Massachusetts, and pyridine-2,6-dicarboxylic acid was from the Aldrich Chemical Company. These reagents were used without further purification.

Complexes of General Formula $Ln(dpc)(dpcH),6H_2O$.—These complexes were prepared for Ln = La, Ce, Pr, Nd, Sm, Gd, and Tb, by mixing hot aqueous solutions of the acetate $Ln(OAc)_3,xH_2O$ (1 mol) and pyridine-2,6-dicarboxylic acid (2 mol), evaporating the solutions to low volume when necessary and allowing the desired products to crystallize at room temperature. The crystals were filtered off, washed with distilled water, absolute ethanol, and diethyl ether, and finally air-dried. The samarium complex $Sm(dpc)(dpcH),6H_2O$ was isolated in two forms. Although we did not ascertain the exact conditions under which each form crystallized, they could readily be differentiated on the basis of their i.r. spectra, that for α-$Sm(dpc)(dpcH),6H_2O$ closely resembled the related spectra of other complexes of the type $Ln(dpc)(dpcH),6H_2O$, but the spectrum of the β-form was quite different (see Results and Discussion section). Analytical data for these complexes are presented in Table 1. The complexes were stable in the air, but partial dehydration readily occurred when they were stored in a desiccator over calcium sulphate.

Complexes of General Formula $Ln(dpcH)_3,H_2O$.—A procedure similar to that described above but using 1 : 3 or 1 : 4 mole proportion of reagents afforded the crystalline complexes $Ln(dpcH)_3,H_2O$ for Ln = Sm, Gd, Tb, Dy, Ho, or Yb. Analytical data for these complexes are presented in

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[1] Part II, A. Anagnostopoulos, R. W. Matthews, and R. A. Walton, *Canad. J. Chem.*, 1972, **50**, 1307.

[2] G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Chem. Soc.* (*A*), 1968, 1108.

[3] M. G. B. Drew, G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Amer. Chem. Soc.*, 1969, **91**, 7769.

[4] M. G. B. Drew, R. W. Matthews, and R. A. Walton, *J. Chem. Soc.* (*A*), 1971, 2959.

[5] H. Gaw, W. R. Robinson, and R. A. Walton, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 695.

Table 1. The reaction of $Nd(OAc)_3$ (1 mol) with pyridine-2,6-dicarboxylic acid (4 mol) was also carried out but only the 1 : 2 complex $Nd(dpc)(dpcH),6H_2O$ was isolated.

Dehydrated Complexes.—When the complexes $Ln(dpc)(dpcH),6H_2O$ (Ln = Ce, Pr, or Gd) and $Dy(dpcH)_3,H_2O$ were heated *in vacuo* at 100 °C for 60 h, the fully dehydrated complexes were formed (Found: C, 35·1; H, 1·8. $C_{14}H_7N_2O_8Pr$ requires C, 35·6; H, 1·5%. Found: C, 38·35; H, 1·8. $C_{21}H_{12}DyN_3O_{12}$ requires C, 38·2; H, 1·8%). The similarity of the i.r. spectra of the cerium, praesodymium and gadolinium complexes confirmed that dehydration to Ce(dpc)(dpcH) and Gd(dpc)(dpcH) had occurred. The absence of a band attributable to ν(O–H) of water in their i.r. spectra showed that dehydration was essentially complete under these conditions.

TABLE 1

Analytical data (%) for hydrated lanthanide(III) complexes of pyridine-2,6-dicarboxylic acid [a]

Complex	Colour	C	H	N
$La(dpc)(dpcH),6H_2O$	White	29·0 (29·1)	3·5 (3·3)	4·5 (4·8)
$Ce(dpc)(dpcH),6H_2O$	Yellow	28·8 (29·0)	3·5 (3·3)	4·6 (4·8)
$Pr(dpc)(dpcH),6H_2O$	Lime green	28·9 (29·0)	3·5 (3·3)	4·6 (4·8)
$Nd(dpc)(dpcH),6H_2O$	Lavender	28·5 (28·8)	3·4 (3·3)	4·55 (4·8)
α-$Sm(dpc)(dpcH),6H_2O$	White	28·4 (28·5)	3·4 (3·2)	4·5 (4·75)
β-$Sm(dpc)(dpcH),6H_2O$	White	28·3 (28·5)	3·4 (3·2)	4·7 (4·75)
$Sm(dpcH)_3,H_2O$	White	37·1 (37·8)	2·3 (2·1)	5·9 (6·3)
$Gd(dpc)(dpcH),6H_2O$	White	28·05 (28·2)	3·4 (3·2)	4·4 (4·7)
$Gd(dpcH)_3,H_2O$	White	37·2 (37·4)	2·3 (2·1)	5·9 (6·2)
$Tb(dpcH)_3,H_2O$	White	37·0 (37·4)	2·2 (2·1)	6·1 (6·2)
$Tb(dpc)(dpcH),6H_2O$	White	27·2 (28·1)	2·3 (3·2)	4·5 (4·7)
$Dy(dpcH)_3,H_2O$	White	37·2 (37·1)	2·25 (2·1)	5·95 (6·2)
$Ho(dpcH)_3,H_2O$	Pink	36·6 (37·0)	2·4 (2·1)	5·9 (6·2)
$Yb(dpcH)_3,H_2O$	White	36·9 (36·6)	2·2 (2·0)	6·0 (6·1)

[a] Theoretical figures are given in parentheses.

TABLE 2

Carbon (1*s*), nitrogen (1*s*), and oxygen (1*s*) binding energies of metal complexes of the pyridine carboxylic acids [a]

Complex [c]	Binding energies in eV [b]		
	C (1*s*)	N (1*s*)	O (1*s*)
Ce(dpc)(dpcH)	288·4; 285·1 (2·3)	399·7 (1·6)	531·9 (1·9)
Pr(dpc)(dpcH)	288·2; 285·0 (2·0)	399·7 (1·75)	531·9 (1·6)
$Dy(dpcH)_3$	287·8; 284·7 (1·8)	399·2 (1·4)	531·6 (2·2)
$Mn(pic)_2,2H_2O$	287·4; 284·4 (2·2)	*e*	*e*
$Mn(quin)_2,2H_2O$	288·0; 284·7 (1·8)	*e*	*e*
$[Mn(pic)_2O]_n$	287·2; 284·1 (1·9)	*e*	*e*
Co(dpc)	286·9; 284·1 (2·1)	*e*	530·7 (1·9)
$Co(nic)_2$	287·6; 284·4 (1·6)	399·4 (2·1)	531·2 (1·9)
$Ni(nic)_2,4H_2O$ [d]	287·1; 284·2 (1·8)	399·1 (2·3)	531·1 (2·3)
$Ni(nic)_2$	*ca.* 287·4; 284·3 (1·9)	399·3 (2·4)	531·2 (2·4)
$Ni(isonic)_2,4H_2O$ [d]	286·9; 284·1 (2·0)	399·0 (2·0)	531·1 (2·1)
$Ni(pic)_2,2H_2O$ [d]	287·2; 284·4 (1·7)	*e*	531·1 (1·8)
$Cu(nic)_2$	287·1; 284·2 (1·8)	399·1 (2·2)	530·8 (2·1)
$Ag^{II}(dpc)(dpcH_2),4H_2O$ [d]	287·2; 284·0 (1·8)	398·7 (1·9)	*e*
$Ag^{II}(lut)_2,2H_2O$	287·5; 284·1 (2·0)	*e*	*e*
$Ag^{I}(pyz\text{-}COO)$	287·2; 285·1 (1·1)	*e*	*e*
$Ag^{I}_2(pyz\text{-}2,3\text{-}COO)$	287·4; 284·9 (1·75)	*e*	*e*

[a] With the exception of the manganese compounds, the powdered samples were dispersed on a gold-plated copper surface. Under these conditions fairly severe charging problems were encountered with the manganese compounds and an acceptable alternative support proved to be a freshly cleaned copper surface. [b] Figures in parentheses are approximate half peak widths. For the carbon 1*s* lines, only the h.p.w. of the more intense line is given. [c] Ligand abbreviations are as follows: picH = picolinic acid; nicH = nicotinic acid; isonicH = isonicotinic acid; quinH = quinolinic acid (pyridine-2,3-dicarboxylic acid); lutH = lutidinic acid (pyridine-2,4-dicarboxylic acid); pyz-COOH = pyrazine-2-carboxylic acid; pyz-2,3-COOH = pyrazine-2,3-dicarboxylic acid. [d] Dehydration of these complexes occurred in the spectrometer. [e] Not measured.

The dehydrated complexes were refluxed with neat pyridine for 90 h but no reaction was observed.

Other Pyridine Carboxylate Complexes.—Several pyridine carboxylate complexes which were required for a comparative study of their *X*-ray photoelectron (p.e.) spectra were prepared by literature methods. These were $Ni(isonic)_2,4H_2O$,[1] $Ni(nic)_2,4H_2O$,[1] $Ni(pic)_2,2H_2O$,[6]* $Ni(nic)_2$,[6] $Cu(nic)_2$,[2] $Ag^{II}(dpc)(dpcH_2),4H_2O$,[2] $Ag^{II}(lut)_2,2H_2O$,[2] $Ag^{I}_2(pyz\text{-}2,3\text{-}COO)$ [7] and $Ag^{I}(pyz\text{-}COO)$.[7] The complex $Mn(pic)_2,2H_2O$ was prepared by a procedure similar to that used for the above nicotinate and isonicotinate complexes (Found: C, 42·2; H, 3·8. $C_{12}H_{12}N_2O_6Mn$ requires C, 43·0; H, 3·6%). Samples of the complexes Co(dpc), $Mn(quin)_2,2H_2O$ and $[Mn(pic)_2O]_n$ were available from an existing source.[8] The abbreviations used for the ligand molecules are given in a footnote to Table 2.

Physical Measurements.—Electronic spectra were recorded on a Cary 14 spectrophotometer. I.r. spectra in the region 4000—400 cm^{-1} were obtained using a Beckman IR 12 spectrophotometer. The p.e. spectra were recorded using a Hewlett–Packard 5950A spectrometer. The aluminium $K_{\alpha1,2}$ line (1486·6 eV) was used as the *X*-ray

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* This complex was readily formed by partial dehydration of the tetrahydrate.

[6] A. Kleinstein and G. A. Webb, *J. Inorg. Nuclear Chem.*, 1971, **33**, 405.

[7] R. W. Matthews and R. A. Walton, *Inorg. Chem.*, 1971, **10**, 1433.

[8] D. L. Hoof, unpublished work still in progress.

excitation source and the powdered samples were usually dispersed on a gold-plated copper surface. The spectra were referenced to the C(1*s*) line of graphite at 284·0 eV. An electrostatic monochromator was used, and a multichannel scanning procedure allowed rescanning of the energy range many times and the successive signals from each increment were scanned until sufficient data were obtained.

X-Ray powder data were collected using a Philips camera (Debye–Scherrer type) and Cu-K_α radiation (λ = 1·5418 Å) with an exposure time of 8—11 h. Traces of the powder photographs were obtained using a Joyce double-beam recording microdensitometer. We are grateful to Dr. W. E. Scott, Biology Department, Purdue University, for his assistance in the use of the microdensitometer.

C, H, and N Analyses were performed by the Purdue University microanalytical laboratory.

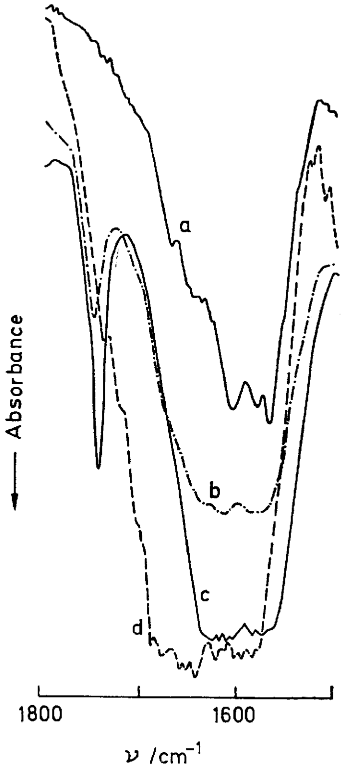

FIGURE 1 I.r. spectra (Nujol mulls) in the 1800—1500 cm^{-1} region; (a), La(dpc)(dpcH),6H_2O; (b), β-Sm(dpc)(dpcH),6H_2O; (c), Ce(dpc)(dpcH); (d), Tb(dpc)$_3$,H_2O

RESULTS AND DISCUSSION

Synthesis and Characterization.—The reaction of the lanthanide acetates Ln(OAc)$_3$,$x$$H_2O$ with pyridine-2,6-dicarboxylic acid in aqueous solution affords two series of complexes. Under the experimental conditions we used, the 1 : 2 complexes Ln(dpc)(dpcH),6H_2O were isolated for Ln = La, Ce, Pr, Nd, Sm, Gd, and Tb whereas Ln (dpcH)$_3$,H_2O resulted for Ln = Sm, Gd, Tb, Dy, Ho, and Yb. Within each series, the compounds appear to be isostructural as judged by the similarity of their i.r. spectra and the close correspondence of the *d*-spacings and relative line intensities of the *X*-ray powder photographs. The i.r. spectra of La(dpc)(dpcH),6H_2O and Yb(dpcH)$_3$,H_2O which are shown in Figure 1 are representative of these two series. The *X*-ray powder data for Pr(dpc)(dpcH),6H_2O, Sm(dpc)(dpcH),6H_2O, Dy(dpcH)$_3$,H_2O, and Ho(dpcH)$_3$,H_2O show that Ln(dpc)(dpcH),6H_2O are not contaminated with Ln(dpcH)$_3$,$_2$O andH *vice versa*.*

These complexes had sufficiently low solubilities in water that we were unable to obtain good quality solution electronic spectra, but the corresponding diffuse-reflectance and Nujol mull spectra were characteristic of the lanthanide(III) ions,[9] and assignments could be made in accord with this assumption. This data, for those lanthanide complexes which show characteristic electronic absorption spectra in the region 6000—26,000 cm^{-1}, together with certain key spectral assignments, has been included in Supplementary Publication No. SUP 20565 (5 pp.).†

The ease with which Ln(dpc)(dpcH),6H_2O were observed to lose water *in vacuo*, led us to study the dehydration of the cerium, praesodymium, and gadolinium complexes. Loss of water was complete when they were pumped *in vacuo* at 100 °C for 60 h. These complexes had i.r. spectra quite different from those of the hydrated species (Figure 1). On the other hand, the dehydration of Dy(dpcH)$_3$,H_2O to Dy(dpcH)$_3$, resulted in very little change in the i.r. spectrum with the exception of the loss of the broad water ν(O–H) band centred at *ca.* 3400 cm^{-1}.

The 1 : 2 samarium complex was isolated in two forms. The α-form had an *X*-ray powder photograph and i.r. spectra typical of other complexes of the type Ln(dpc)(dpcH),6H_2O. However, the β-form, although possessing a powder photograph very similar to that of the α-form, had an i.r. spectrum (Figure 1), which with the exception of a very broad intense water band centred at 3300 cm^{-1}, resembled closely the spectra of the dehydrated species Ln(dpc)(dpcH) but with the following differences: several of the absorption bands of β-Sm(dpc)(dpcH),6H_2O were significantly broader than those of Ln(dpc)(dpcH) and there were some slight differences in relative band intensities.

Structural Considerations.—The ease with which Dy(dpcH)$_3$,H_2O is dehydrated to Dy(dpcH)$_3$ and the absence of an accompanying change in the 1700—1500 cm^{-1} region of the i.r. spectrum, where the diagnostic ν(C–O) vibrations are clearly distinguishable, implies that this complex is not $(H_3O)^+$Dy(dpc)(dpcH)$_2$. Accordingly, we formulate the 1 : 3 derivatives as nine-coordinate complexes containing three monoanionic terdentate (dpcH) molecules. We have recently shown from a three-dimensional *X*-ray structure analysis of the nickel(II) complex Ni(dpcH)$_2$,3H_2O,[5] that the two equivalent ligand molecules bond in this fashion. As expected, there is a modest disparity in the Ni–O

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* Details of the i.r. spectra and *X*-ray powder data not presented here are available on request to R. A. W.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20. (Items less than 10 pp. are supplied as full size copies.)

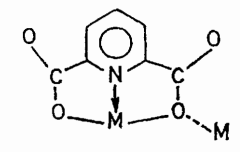
[9] See for example, J. Selbin, N. Ahmad, and N. Bhacca, *Inorg. Chem.*, 1971, **10**, 1383.

distances within each Ni(dpcH) moiety, but this does not result in any severe distortions of the co-ordinate geometry.* Furthermore, a recent structure analysis of the complex $Na_3[Yb(dpc)_3],14H_2O$,[10] has shown that the central ytterbium atom is nine-co-ordinate and is bound to three equivalent dianionic terdentate (dpc) molecules. The derivatives $Ln(dpcH)_3,H_2O$ which we have isolated and characterized, are accordingly best considered as close structural analogues of the $[Ln(dpc)_3]^{3-}$ anions.[10]

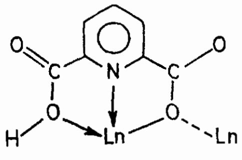
The spectral properties and *X*-ray powder measurements on $Ln(dpc)(dpcH),6H_2O$ provide no direct information on their detailed stereochemistry. However, the isolation of two forms of the samarium complex which possess similar *X*-ray powder photographs but dissimilar i.r. spectra allows us to draw several tentative conclusions concerning the possible structures of these derivatives. The most striking spectral difference between the α- and β-forms is the presence of a single sharp band of medium intensity at 1750 cm^{-1} in the i.r. spectrum of β-$Sm(dpc)(dpcH),6H_2O$ which we assign to a 'free' ν(C=O) mode. Since the latter spectrum (1800—400 cm^{-1}) closely resembles that of the anhydrous complexes Ln(dpc)(dpcH), (Figure 1), it suggests that the water molecules are not co-ordinated to the central samarium atom in the β-complex. Also, the close similarity of the *X*-ray powder photographs of β-$Sm(dpc)(dpcH),6H_2O$ and the other derivatives of the type $Ln(dpc)(dpcH),6H_2O$ in turn indicates a structural similarity, so that for the latter species we also conclude that the water molecules are present as 'lattice' water. This is also borne out by the ease with which these water molecules are lost *in vacuo*.

While only a single-crystal *X*-ray analysis can provide unambiguous structural data, we can account for the above observations in terms of a nine-co-ordinate stereochemistry about the lanthanide atoms. A recent structure analysis on the copper(II) complex $Cu(dpc),2H_2O$[11] has shown that the dianionic ligand molecule is capable of bridging between metal centres as shown in structure (I).

Accordingly, for β-$Sm(dpc)(dpcH),6H_2O$ and the dehydrated species Ln(dpc)(dpcH), all of which show a well resolved band at *ca.* 1750 cm^{-1} in their i.r. spectra assignable to ν(C=O) of an uncomplexed C=O group, we propose a polymeric structure, in which polymerization is achieved *via* the three carboxylate oxygen atoms bound to each metal centre. The environment about the lanthanide atom would therefore comprise two nitrogen atoms, three carboxylate oxygens from the molecules (dpc) and (dpcH), one carboxylic acid oxygen from (dpcH) and a further three carboxylate oxygens bridging from adjacent molecules. For α-$Sm(dpc)(dpcH),6H_2O$ and the other complexes $Ln(dpc)(dpcH),6H_2O$, a similar structure but with C=O co-ordination from the carboxylic acid group is proposed. These differences are shown in structures (II) and (III).

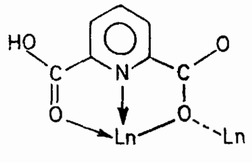


(I)



(II)

(II), β-$Sm(dpc)(dpcH),6H_2O$ and anhydrous Ln(dpc)(dpcH) (Ln = Ce, Pr, or Gd)



(III)

(III), α-$Sm(dpc)(dpcH),6H_2O$ and $Ln(dpc)(dpcH),6H_2O$ (Ln = La, Ce, Pr, Nd, Gd, or Tb)

The failure of the anhydrous complexes to react with pyridine certainly points to them being co-ordinatively saturated, as would be the case for the proposed polymeric nine-co-ordinate structures. Furthermore, it seems reasonable for the isomerization depicted in (II) and (III) to occur, and if this is the only difference between the α- and β-forms of the samarium complex then this could account for the similarity of their *X*-ray powder photographs.

X-Ray Photoelectron Spectra.—The *X*-ray p.e. spectra of the anhydrous complexes Ln(dpc)(dpcH) (Ln = Ce or Pr) and $Dy(dpcH)_3$ were investigated to assess whether this technique could provide definitive structural information on these species. The anhydrous complexes rather than the hydrates were chosen for this study since with the latter, dehydration occurred in the spectrometer under the high vacuum conditions of the experiment. Carbon, nitrogen, and oxygen (1*s*) binding energies for the above complexes are given in Table 2 and the spectrum of Ce(dpc)(dpcH) is shown in Figure 2. In addition, we recorded the related spectra of a variety of other pyridine carboxylate complexes for comparative purposes. This data is also collected in Table 2. Since no special precautions were taken to eliminate sample charging effects, modest differences in binding energies and peak widths between the different complexes are not necessarily significant. With the data at hand, the following conclusions are possible.

(*i*) Two well separated carbon lines are seen in the spectra of all the complexes listed in Table 2, at binding energies comparable to those observed for the benzene carboxylic acids.[12] The line at highest binding

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* An independent structure analysis of $Ni(dpcH)_2,3H_2O$ has confirmed our results (Professor M. Nardelli, personal communication to R. A. W.). Further, this latter study has located the hydrogen atoms associated with the two 'protonated' carboxylate groups.

[10] J. Albertsson, *Acta Chem. Scand.*, 1970, **24**, 1213.

[11] M. Biagini Cingi, A. Chiesi Villa, C. Guastini, and M. Nardelli, *Gazzetta*, 1971, **101**, 825.

[12] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, 'ESCA; Atomic, Molecular and Solid State Structures Studied by Means of Electron Spectroscopy,' Almquist and Wiksells, Uppsala, 1967, p. 78.

energy is associated with the carboxylate carbon atoms. For the lanthanide complexes, the ratio $C_{(COO)} : C_{(C_5H_3N)}$ was close to 2 : 5, confirming that decarboxylation had not occurred and that the ligand molecules were intact.

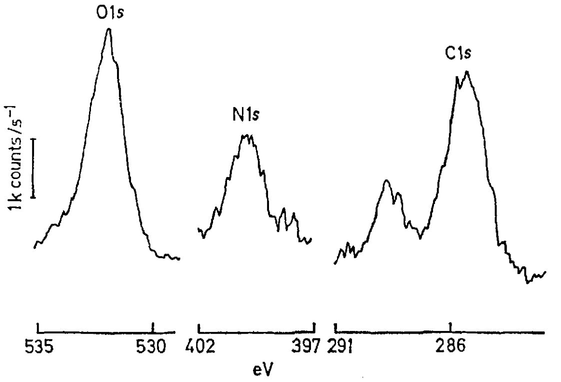

FIGURE 2 Oxygen (1*s*), nitrogen (1*s*), and carbon (1*s*) *X*-ray p.e. spectra of Ce(dpc)(dpcH)

(*ii*) The half peak widths of the N (1*s*) lines of the lanthanide complexes ranged from 1·4 to 1·8 eV, and gave no hint of the presence of nitrogen atoms in different environments, so that we can rule out the presence of unco-ordinated nitrogen atoms.

(*iii*) No distinction was possible between the oxygen atoms. This was not unexpected since there are unlikely to be significant differences in charge on the oxygen atoms in the $-COOH$ and $-COO^-$ groups.[13]

(*iv*) No significant differences were observed between the spectra of Ln(dpc)(dpcH) and $Dy(dpcH)_3$.

(*v*) Attempts to observe the 4*s* lines of the lanthanides were unsuccessful. Our original hope had been to see whether multiplet splittings, due to interaction of the *s* shell with the partly filled 4*f* shell, could be observed in these systems as has previously been found for LnF_3.[14] Our failure to observe these lines can probably be attributed to the relatively low proportion of the desired element in these compounds (less than 30%); for LnF_3 the lanthanides are present in excess of 70% of the formula weight.

We thank the National Science Foundation and the Advanced Research Projects Agency, administered through the Purdue University Material Science Council, for support of this research. One of us (R. A. W.) gratefully acknowledges support from the Camille and Henry Dreyfus Foundation. Dr. D. P. Murtha and Mr. J. Sheets kindly provided samples of the cobalt, nickel, copper, and silver complexes.

[2/1618 *Received*, 10*th July*, 1972]

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[13] Ref. 12, p. 120 and 121.

[14] R. L. Cohen, G. K. Wertheim, A. Rosencwaig, and H. J. Guggenheim, *Phys. Rev. B*, 1972, **5**, 1037.