Inorganica Chimica Acta, 63 (1982) 225–231

Ni(II) Chromophores with the 2,6-Bis(diphenylphosphinomethyl)pyridine Ligand:
XPS Characterization of the Electronic Structure

M. V. ANDREOCCI, G. MATTOGNO, R. ZANONI
Institute of General and Inorganic Chemistry, University of Rome, Rome, Italy

P. GIANNOCCARO and G. VASAPOLLO
Institute of General and Inorganic Chemistry, University of Bari, Bari, Italy

Received April 7, 1982

XP spectral data are reported for Ni, N, P and L atoms (L = ligand Cl^-, NO_3^-, ClO_4^-, NCS^-*) in the chromophores of Ni/(PNP) complexes ((PNP) = 2,6-(bis(diphenylphosphinomethyl))pyridine ligand), and the structural implications are discussed. Quadratic [Ni(PNP)L] chromophores are well characterized through low Ni2p b.e. values and covalent XP spectral patterns of L ligands.* $Ni(PNP)(NCS)_2$ *reveals a well defined presence of [Ni(PNP)(NCS)] quadratic chromophores, as well as of more ionic* NCS^- *ligands, possibly contained in pseudooctahedral* $[Ni(PNP)(NCS)_3]^-$ *environments as suggested by previous investigations. Definite evidence is presented for the occurrence of two inequivalent (PNP) ligands in cationic* $[Ni(PNP)_2]^{2+}$ *species, one terdentate with bonded N, and one bidentate with non-coordinated pyridine nitrogen.*

Introduction

The 2,6-bis(diphenylphosphinomethyl)pyridine (PNP) ligand is well known for its ability to bind to metals giving rise to different stereochemistries [1, 2], some of which are not yet fully characterized. We undertook therefore an XPS investigation of some Ni(II) complexes with the (PNP) ligand, which were already prepared and investigated by other techniques by some of us [2, 3]. The use of the XPS technique is intended as a means to obtain additional evidence for the electronic and steric structure of the investigated complexes. Although sometimes not very accurate in detecting structural effects (*e.g.* only small b.e. differences between high- and low-spin Ni(II) complexes [4, 5]), the XPS technique is nevertheless able to give unique information (through inner-core orbital energy values and their chemical shifts) on trends of atomic charge within the metal chromophores. In addition XPS, as a surface technique, allows the detection of surface changes in chemical composition with respect to bulk, hence of surface reactivity effects.

In the case of our (PNP) complexes of Ni(II), we expected to obtain first of all evidence for differences in chemical composition between bulk and surface in the solids; data which can be referred to the bulk are expected to lend further support to already proposed stereochemical arrangements, and to suggest trends of atomic charge distribution within the chromophores, and possibly help in assigning dubious cases.

As an aid to structural assignments, we performed approximate molecular orbital calculations by an extended Hückel method [6], and systematically compared trends in experimental b.e. values with trends in computed atomic charges.

Experimental

The investigated complexes include [Ni(PNP)Cl]Cl, $[Ni(PNP)Cl]ClO_4$, $[Ni(PNP)(NCS)]ClO_4$, $Ni(PNP)(NCS)_2$, $[Ni(PNP)(NO_3)_2]$, $[Ni(PNP)_2](NO_3)_2$ and $[Ni(PNP)_2](ClO_4)_2$, besides the free (PNP) ligand, prepared according to [1, 2, 3] and characterized to analytical purity by their physical constants [1, 3].

XPS measurements were performed on a VG ESCA-3 spectrometer equipped with $AlK\alpha_{1,2}$ source (1486.7 eV). Samples were dusted onto solid gold bearing plates at room temperature: reported data are averages of no less than three different samplings, each repeated three times, with standard deviations in the range 0.2 eV. Radiation damage was negligible under the employed experimental conditions, and cooling of samples to liquid N_2 temperature caused

0020-1693/82/0000-0000/$02.75

TABLE I. Structural Data.

Geometrical data	Bond lengths (Å)		Bond angle (°)
Pyridine ring C–C(C–N)	1.39		120
C–H	1.09		120
C–CPh_2	1.52		120
		H–C–H	109
C–P	1.76	C–C–P	109
P–H	1.43	H–P–H	98.7
$[Ni(pnp)Cl_{(1)}]^+Cl_{(2)}$			
Ni–N	2.0(1.795)[a]	P–Ni–N	90
Ni–P	~2.2(2.183)		
Ni–$Cl_{(1)}$	2.3	P–Ni–Cl	90
Ni–$Cl_{(2)}$	3.5(2.5)	pseudopentacoordination	
$[Ni(pnp)N_{(2)}CS]N_{(3)}CS$			
Ni–$N_{(2)}$	2.0		
$N_{(2)}$–C	1.22		
C–S	1.56		
Ni–$N_{(3)}$	2.0 (2.2; 2.5)		
$[Ni(pnp)_1(pnp)_2]^{++}$		pseudopentacoordination	

[a] Values in parentheses indicate the various calculations performed which gave comparable trends in atomic charges.

no detectable spectral change. B.e. measurements are referenced to $Au4f_{7/2}$ at 84.0 eV, and surface charging effects compensated by referring to contamination Cls peaks taken as 285.0 eV. Gaussian peak shape was assumed in p.e. band deconvolution.

Approximate prediction of atomic charges was performed on the basis of m.o. EHT calculations [6]. As for the assumed molecular geometry, the PNP ligand has no experimentally determined structure, so that a model molecule has been built with known bond distances and angles of related smaller molecules, and substituting the phenyl groups of the PPh_2 moieties, with H atoms. A trial geometry of the molecule, in the planar conformation suitable to form planar complexes, has been partly optimized by MNDO calculations [6c]. The final structural data are reported in Table I, together with the other lengths assumed in the complexes. The EHT parameters were taken from ref. 6b: for sulphur, which does not appear in this reference, we used the following values: $H_{ii}(3s) = -23.72$ eV; $H_{ii}(3p) = -12.5$ eV; exponent (sp) = 1.90.

Results

In the free PNP ligand the b.e. values are 398.9 and 130.9 eV for N1s and $P2p_{av}$ respectively, values which are indicative of partial negative charge and which are related to $q_N = -0.95$ e and $q_P = -0.20$ e, predicted by EHT computations (see Table II).

Square planar cationic complexes, sometimes with possible weak 5-coordination in square pyramidal apical positions, are expected to occur in $[Ni(PNP)Cl]^+Cl^-$, $[Ni(PNP)Cl]^+ClO_4^-$ and $[Ni(PNP)(NCS)]^+ClO_4^-$, which show remarkable similarities in their XP spectral behaviour.

Ni 2p ionization patterns show low-intensity satellites about 7.5 eV from the main peaks: these are not normally expected for low-spin Ni(II) compounds, and represent an unusual feature in completely diamagnetic metal systems. By coincidence, the $K\alpha_{3,4}$ satellites of the $2p_{1/2}$ peak are expected in the same region as the satellites on the high b.e. side of $Ni2p_{3/2}$, but their expected intensity (~11% [7]) is too low to account for the whole of the observed satellites (~15–30% of the main peak). Monopole shake-up transitions cannot be excluded, although they are not of general occurrence with low-spin Ni(II) systems. The actual intensity of the observed satellites is not reproducible and varies to some extent, depending on sample preparation, ageing, air exposure, *etc.* Therefore, the most likely assignment of the observed satellite structures is to some paramagnetic byproduct, which, if concentrated in the outermost surface layers, can escape analysis by bulk methods, although a contribution from genuine low-intensity shake-up satellites of the main low-spin species cannot be ruled out, the possible occurrence of such satellites being still controversial in the literature.

We conclude that in the above Ni(II)–PNP species a significant but not very intense presence of high-spin byproducts is likely to occur, particularly at the surface, but on the whole the XPS evidence reflects the low-spin bulk structure suggested by previous evidence [1–4] for the above compounds on the ground of either a true quadratic (chromophore [Ni(PNP)X]) or a square pyramidal [Ni(PNP)X]Y structure.

The bulk structure of the above species is characterized, on XPS evidence, by chemical shifts on the donor atoms N and P of the (PNP) ligand, to 400.2 ± 0.2 and 131.7 eV respectively, against 398.9 and 130.9 eV in the free ligand: such shifts are consistent with the donor effect expected on complex formation, and are paralleled by a decrease of negative charge predicted by EHT computations (*ca.* 0.6–0.7 e charge donation from N, and *ca.* 0.59 e from P). The b.e. shift on N is larger than on P, because of a possible larger back-donation effect from Ni onto P, and also because of the much smaller slope of b.e. variation with q_P [8]. Furthermore, the b.e. values for coordinatively bonded P and N in the (PNP) ligand are almost constant for all Ni complexes investigated here, irrespective of spin state, coordination geometry and the nature of extra ligands, indicating that the donor interaction between the (PNP) donor sites and the Ni center is the dominating effect in determining atomic charge distribution within the chromophore. This situation is again reproduced by EHT calculations, which predict q_P remarkably constant at +0.39–0.40 e, and q_N only slightly varying between *ca.* –0.20 e and –0.33 e in ligated (PNP).

Ni $2p_{3/2}$ b.e. falls at 855.2 ± 0.2 eV in the above series, and is therefore to be regarded as essentially constant (within experimental error), the value being typical of square planar chromophores containing the (PNP) ligand (possibly with weak apical pyramidal coordination in [Ni(PNP)Cl](Cl).

Further noteworthy aspects of the characterization of the electronic structure of the above chromophores lie in the N1s signals in $[Ni(PNP)(NCS)]^+ClO_4^-$ which are clearly double, with component peaks at 400.3 eV (PNP) and 398.7 eV (NCS^-), for which a charge q_N of a –0.93 e is predicted by EHT calculations; this again confirms the q_N/b.e. relationship suggested by the comparison between bonded and non-bonded N in the (PNP) ligand, and gives $(N1s)-(S2p)_{av}$ = 236.1 eV, as expected for N-coordinated thiocyanate in perfect agreement with the empirical regularity reported in a previous work [9]. Cl signals are consistent with the presence of two inequivalent chlorine species in $[Ni(PNP)Cl]ClO_4$, ($Cl2p_{av}$ in ClO_4^- = 208.3 eV) and [Ni(PNP)Cl]Cl (197.3 eV for the outer Cl atom), whereas covalently bonded Cl within the quadratic Ni(II) chromophores has $2p_{av}$ b.e. at 199.0 eV. This is in qualitative agreement with EHT calculations, which predict a relatively low negative charge for covalently bonded Cl within the quadratic chromophore (–0.3 e), whereas the second Cl atom is expected to be substantially more negative, even if weakly coordinated in pyramidal apical position. The quantitative inaccuracy of EHT predictions does not allow us to establish with certainty whether the outer chlorine atom is a fully external counterion, or lies in weak 5-coordinated position. As a whole, XPS evidence supports the high stability of the electronic structure of the quadratic chromophores [Ni(PNP)X], where the steric structure of the (PNP) ligand matches very closely, on the ground of our planar model structure, the steric requirements for formation of quadratic [Ni(PNP)X] chromophores.

$Ni(PNP)(NO_3)_2$ is another structural type, classified on the ground of previous results as a pseudo-octahedral high-spin species with $[Ni(II)(PNP)O_3]$ chromophore (two bidentate and one monodentate NO_3^- ligands in the coordination sphere). Such structure is reflected and confirmed by the Ni2p p.e. patterns, with $2p_{3/2}$ peak at 855.9 eV, accompanied by intense satellites (ΔE = 6.5 eV). The b.e. is slightly higher than for $[Ni(PNP)X]^+$ quadratic chromophores, and is in keeping with the expected larger ionicity of coordination bonds in the high-spin species, although the trend is not generally followed by other (PNP) complexes, and is not directly comparable with data for Ni(II) complexes in other environments. There are two N1s signals well apart (intensity ratio 1:2), assigned as ligand N (at 400.1 eV as typical of coordinated (PNP)) and nitrate (at 407.4 eV). Since the proposed structure of $[Ni(PNP)(NO_3)_2]$ [2, 3] comprises one bidentate and one monodentate coordinated nitrate, the two nitrate nitrogen atoms are expected to be inequivalent, and might give rise to two different b.e. signals. Actually only one rather narrow band is distinguishable, so the inequivalence due to different bonding modes has only small, practically undetectable effects on the N1s b.e. Rather, the average b.e. of 407.4 eV is higher than in free (ionic) nitrates (*e.g.* $[Ni(PNP)_2](NO_3)_2$, see below), in agreement with a general involvement of the NO_3 moieties in the donor effect towards the metal center. On the whole, $[Ni(PNP)(NO_3)_2]$ presents the typical XPS patterns of high-spin pseudooctahedral species, with the relevant feature of intense and reproducible shake-up satellites on Ni2p ionization bands, while no significant b.e. shift on Ni2p b.e. are observed with respect to low-spin Ni–PNP species.

Less obvious is the interpretation of the XP spectral patterns of $Ni(PNP)(NCS)_2$, for which dif-

TABLE II. Electronic Structure Data.

	Ni		N		P		Cl	
	$2p_{3/2}$ b.e. (ΔE satellites)	q_{Ni} (EHT)	1s b.e.	q_N (EHT)	$2p_{av}$ b.e.	q_P (EHT)	$2p_{av}$ b.e.	q_{Cl} (EHT)
(PNP) free ligand	–	–	398.9	−0.95	130.9	−0.20	–	–
[Ni(PNP)Cl]Cl	855.0 (7.7)	−0.09	400.0	−0.27	131.6	+0.39	197.3 (ion.) 199.0	−1 −0.57
[Ni(PNP)Cl](ClO_4)	855.2	−0.09	400.4	−0.27	131.7	+0.39	199.0 208.1	−0.57 (ClO_4^-)
[Ni(PNP)(NCS)](ClO_4)	855.5 (7.5)	−0.10	398.7 400.3	−0.93 (NCS^-) −0.33 (PNP)	131.7	+0.38	208.3 $S2p_{av}$ 162.6	(ClO_4^-) −0.36
Ni(PNP)$(NCS)_2$	855.5 (7.0)		$398.0\left\{\begin{matrix}397.6\\398.6\end{matrix}\right\}$ 400.1	NCS^- (PNP)	131.4		$S2p_{av}$ 162.6	
[Ni(PNP)$(NO_3)_2$]	855.9 (6.5)		400.1 407.4	(PNP) (NO_3)	131.6			
$Nipy_4(NCS)_2$	855.2 (3.7/7.5)		398.0 bond.				$S2p_{av}$ 162.8	
$[Ni(PNP)_2](NO_3)_2$	855.7		$400.0\left\{\begin{matrix}399.2\\400.8\end{matrix}\right.$ 406.7	−0.94 (PNP) free −0.42 (PNP) bond. (NO_3^-)	132.0	+0.43 (bond.) −0.20 (free)		
$[Ni(PNP)_2](ClO_4)_2$	855.7 (7.5)		$399.8\left\{\begin{matrix}399.1\\400.4\end{matrix}\right.$	−0.94 (PNP) free −0.42 (PNP) bond.	132.0	+0.43 (bond.) −0.20 (free)	208.2	(ClO_4^-)

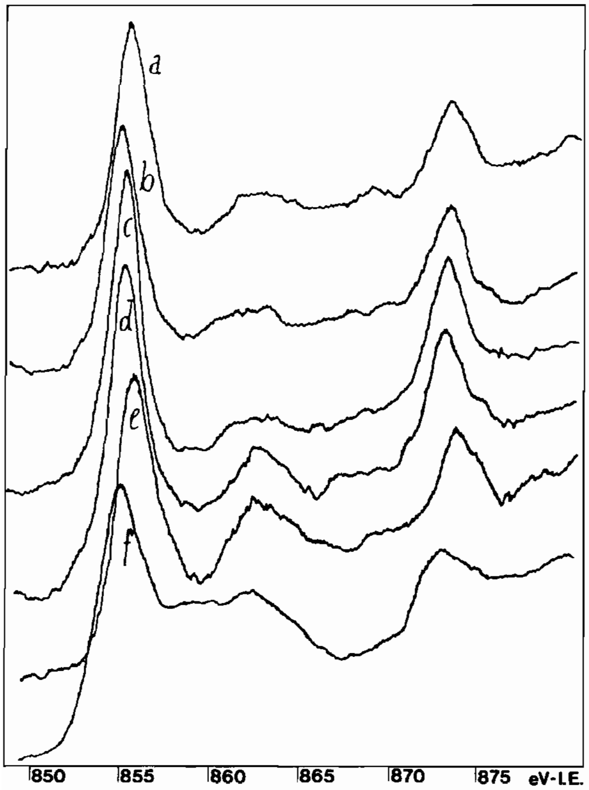

Fig. 1. Ni2p XP spectra of: a) $[Ni(PNP)_2](NO_3)_2$, b) $[Ni(PNP)Cl](ClO_4)$, c) $[Ni(PNP)(NCS)](ClO_4)$, d) $Ni(PNP)(NCS)_2$, e) $[Ni(PNP)(NO_3)_2]$, f) $Nipy_4(NCS)_2$.

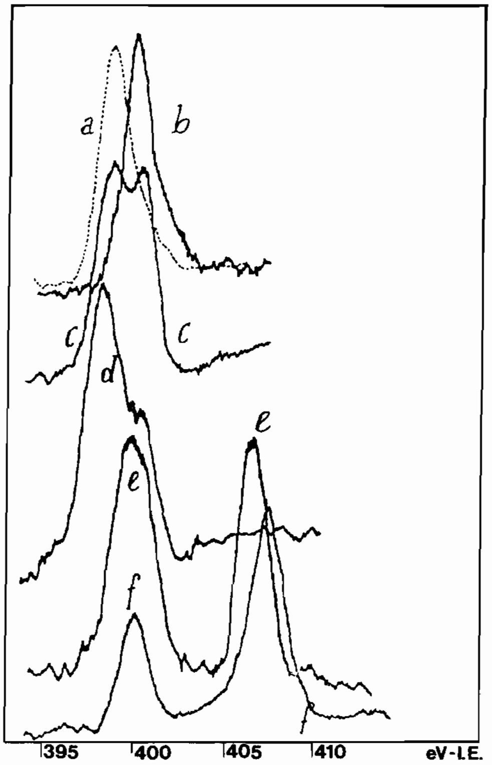

Fig. 2. N1s XP spectra of: a) (PNP) free ligand, b) $[Ni(PNP)Cl](ClO_4)$, c) $[Ni(PNP)(NCS)](ClO_4)$, d) $Ni(PNP)(NCS)_2$, e) $[Ni(PNP)_2](NO_3)_2$, f) $[Ni(PNP)(NO_3)_2]$.

ferent structures have been proposed [1, 3] in the literature. The most recent studies [3] present convincing evidence for a double salt structure $[Ni(PNP)(NCS)]^+[Ni(PNP)(NCS)_3]^-$ in the bulk of the solid, with half diamagnetic and half paramagnetic nickel(II) moieties. Nevertheless, easy structure distortions (particularly on the surface) would not be surprising. XP spectral patterns first of all give direct evidence for the existence of quadratic $[Ni(PNP)(NCS)]^+$ moieties on the surface of solid $Ni(PNP)(NCS)_2$, since they resemble rather closely the case of $[Ni(PNP)(NCS)]^+ClO_4^-$. As evident from Fig. 1 and Table II, $Ni2p_{3/2}$ peaks are accompanied by satellites whose intensity is somewhat higher than those of $[Ni(PNP)(NCS)]^+(ClO_4)^-$ (where they are assigned to paramagnetic impurities), and still lower than those of fully paramagnetic species such as $[Ni(PNP)(NO_3)_2]$ or $Nipy_4(NCS)_2$, measured for comparison and reported in Table II and Fig. 1. The $Ni2p_{3/2}$ b.e. value of 855.5 eV is not particularly significant for structural assignments: one might argue that it is halfway between the lowest limit of $[Ni(PNP)X]^+$ diamagnetic species and the high-spin species $[Ni(PNP)(NO_3)_2]$, but the involved energy differences are not much larger than experimental uncertainty, and the 2p peaks in $Ni(PNP)(NCS)_2$ are fairly narrow and not indicative of the presence of distinctly inequivalent species in the XPS sampling region. More informative are N1s XP spectral data, since the N1s band has a composite profile, which can be resolved into two components (intensity ratio 1:2, peaks at 400.1 and 398.0 eV), the first of which is related to (PNP) nitrogen, and the second one to NCS^-. The second component is still broad (even allowing for the larger uncertainty in deconvoluted component bands), and can be further resolved into two sub-bands peaked approximately at 198.6 (hence virtually identical with $[Ni(PNP)(NCS)]^+(ClO_4)^-$; Δ = N1s b.e. – S2p b.e. = 236.0 eV) and 397.6 eV (Δ = 235.0 eV); the latter value is close to the case of NCS^- bonded to Ni(II) in the paramagnetic environment of $Ni(py)_4(NCS)_2$, although an accurate assignment is not possible since $Ni(py)_4(NCS)_2$ exhibits a N1s band with a maximum at about 398.0 eV, which is rather broad and contains contributions from both pyridine and thiocyanate nitrogens. The b.e. difference N1s–S2p is as low as 235.0 eV for the second component of $Ni(PNP)(NCS)_2$, so also an assignment to ionic or S-bonded thiocyanate would be possible on the ground of XPS evidence alone [9]. The extra CNS^- with respect to $[Ni(PNP)(NCS)]^+(ClO_4)^-$ appears therefore as if it were, at the surface, in a binding position retaining ionic character, possibly compatible with a $[Ni(PNP)(NCS)]^+(NCS)^-$ formulation, and most plausibly leading to alternate bonding to [Ni(PNP)(NCS)] equatorial moieties and eventually resulting in $[Ni(PNP)(NCS)]^+ \cdots [Ni(PNP)(NCS)_3]^-$ sequences (particularly in the deep layers). EHT calculations suggest a high negative charge on N in ionic thiocyanate, which would imply a lower b.e. than actually observed; therefore a model of bridging or loosely coordinated thiocyanate appears more plausible. XP spectral patterns of N1s ionization seem to present evidence for equatorially bonded thiocyanate (both in planar $[Ni(PNP)(NCS)]^+$ and in pseudooctahedral $[Ni(PNP)(NCS)_3]^-$ units), against axial NCS^- ligands in octahedral environment. The picture of surface structure suggested by XPS evidence therefore confirms once again the stability and well defined characterization of the quadratic $[Ni(PNP)X]^+$ chromophores, while giving less clear-cut evidence for $[Ni(PNP)(NCS)_3]^-$ pseudooctahedral moieties, and even implying a possible dissocation of the latter moieties near the surface of solid $Ni(PNP)(NCS)_2$.

The divalent cationic complexes $[Ni(PNP)_2]^{2+}(Y^-)_2$ ($Y^- = NO_3^-$, ClO_4^-) have been previously characterized as low-spin species, where electronic absorption spectra and other experimental data seem to rule out however a simple quadratic coordination of $[NiP_4]$ or $[NiP_3N]$ type [3]. One can easily expect, on the ground of the favorable steric arrangement of the planar [PNP] unit in the PNP ligand, that one ligand would bind in a facile way to Ni(II) as in all previously observed $[Ni(PNP)X]^+$ species, leaving the second ligand with the role of a monodentate phosphine (chromophore $[NiP_3N]$); however, chemical evidence shows that there is no free pending phosphine end in solutions of $[Ni(PNP)_2]^{2+}$, so the structure should be more complex. The XP spectra yield some support to the above assumption, although they are not able to indicate unequivocally the actual stereochemistry of coordination. Ni2p signals are accompanied by weak satellites, again pointing to surface presence of some paramagnetic by-product, much as in the case of $[Ni(PNP)X]^+$ species, except that the intensity of satellites (hence the surface concentration of possible impurities) is here even lower. On the whole however the spectral patterns of Ni ionization are consistent with a low-spin, essentially diamagnetic structure: the $2p_{3/2}$ b.e. value is relatively high (855.8 ± 0.1 eV) for low-spin Ni(II) species, possibly in part as a consequence of the higher positive charge (+2) residing on the molecular unit which contains the chromophore.

The N1s spectrum shows a broad band around 400 eV (besides the nitrate band at 406.7 eV for Y = NO_3), clearly comprising two components, which reveals the presence of inequivalent nitrogen atoms in the $[Ni(PNP)_2]^{2+}$ units, and can be deconvoluted typically at 399.1 and 400.4 eV (for Y = ClO_4), *i.e.* to values corresponding to complexes and free nitrogen of the (PNP) ligand. The obvious implication is that the two (PNP) ligands are unequivalent, and that one (PNP) ligand coordinates again to Ni(II) in the sterically favored planar arrangement occurring in all previous cases, while the second ligand is certainly bonded to Ni(II) through at least one of its phosphorus atoms (thus completing a minimum c.n. of four) and having its nitrogen atom non-coordinated by virtue of steric requirements.

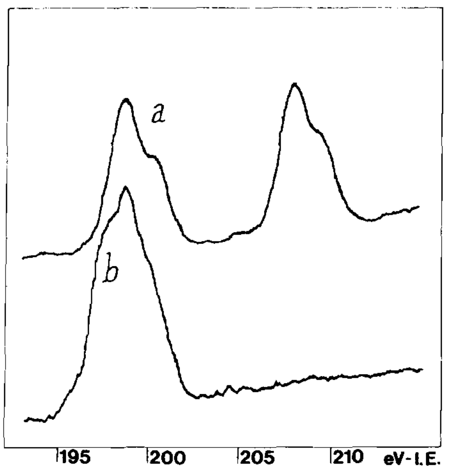

Fig. 3. Cl2p XP spectra of: a) $[Ni(PNP)Cl](ClO_4)$, b) [Ni(PNP)Cl]Cl.

The actual situation of the other P atom in the second ligand is not identified by XPS evidence, since the P2p bands are not informative to this regard: the P2p signal peaks at 132.0 eV (a few tenths of eV above the average of the previous cases; like the Ni2p and N1s signals, this might be due to the high positive charge of the chromophore-containing cationic unit), and is still rather narrow, *i.e.* without evident indication of presence of strongly inequivalent phosphorus atoms. Actually, the b.e. difference between bonded and non-bonded phosphines is small enough to seriously impair detection of one non-bonded P atom in the presence of three bonded ones, but the small width of the observed P2p band makes the latter hypothesis implausible. XPS data appear therefore compatible both with a pseudo-trigonal bipyramidal and with a highly distorted square pyramidal structure, the former structure being favored by data from other investigation techniques [3].

Discussion

X-ray photoelectron spectroscopy (XPS) proves useful in contributing to the elucidation of the steric and electronic structure of different types of Ni(II) complexes with the (PNP) ligand. Although not able by itself to solve completely their structures, its use provides support to previous structural hypotheses, as well as further hints for still unsolved problems. It also allows detection and possible explanation of surface effects (distortions, structural modifications, formation of surface species), and semiquantitative correlations with atomic charge distribution, also in comparison with EHT calculations. Specifically, the present study of XPS characterization suggests the presence of paramagnetic contaminating species often occurring in low-spin [Ni(PNP)X]Y complexes, even if in low concentration so as to escape bulk analysis; besides, evidence was obtained for a strong characterization of quadratic [Ni(PNP)(NCS)] units in the complicated structure of Ni(PNP)(NCS)$_2$.

Chemical shifts of inner core b.e. values, expected to give information about coordinated or uncoordinated situations, occurrence of inequivalent sets of atoms and trends of charge distributions, are relatively small for the measured signals of Ni (differing only slightly betweee high- and low-spin Ni species) and of P; more informative are the XP spectra of Cl and N which not only allow differentiation of electronic structures in vastly different chemical environments (such as coordinated and uncoordinated N in the (PNP) ligand, inner- and outer-sphere chlorine, and nitrogen in thiocyanate, pyridine ring and nitrate), but which also allow detection of more subtle effects such as those observed in the different Ni(II) environments occurring in the surface structure of Ni(PNP)(NCS)$_2$. Correlations between observed b.e. shifts and computed (EHT) values of atomic charge work satisfactorily at a semiquantitative level, and help considerably both in solving problems of structural assignment and in contributing to the general picture of the electronic structure of the investigated chromophores.

Most of our b.e. data on N1s and (P, S, Cl)2p are in good agreement with the standard values and the ratios of slopes given by Larsson [8]; quantitatively, the slopes deduced from our data and our computed (EHT) values are smaller by a factor of 3–4 than the values quoted by Larsson [8], a fact which can be due either to neglect of potential terms of neighbouring Madelung effects, or to overestimates of atomic charges by our EHT method (or both).

The most relevant fundamental factor of the structure of Ni (PNP) complexes emerging from analysis of the XPS results is the strong characterization and stability of the quadratic steric arrangement of the [Ni(PNP)X] units, probably deriving from the favorable steric requisites of the (PNP) ligand for chelation on a Ni(II) centre. Such structural units can appear isolated (X = Cl, NCS), or act as the basis for construction of more complex structures. This is the case for X = (PNP) where the rest of the second (PNP) ligand modifies presumably the steric arrangement, or for insertion of nitrate oxygen into the enlarged coordination sphere to give high-spin [Ni(PNP)(NO$_3$)$_2$], or for insertion of further NCS$^-$ ligands into the enlarged coordination sphere to give the high-spin structures reported for solid Ni(PNP)(NCS)$_2$.

Acknowledgement

The present work has been carried out with financial support from the C.N.R.

References

1 W. V. Dalhoff, G. H. Ford and S. M. Nelson, *J. Chem. Soc. (A)*, 388 (1971).
2 P. Giannoccaro, G. Vasapollo and A. Sacco, *Chem. Comm.*, 1136 (1980).
3 P. Giannoccaro, G. Vasapollo, C. F. Nobile and A. Sacco, *Inorg. Chim. Acta*, in the press (1982).
4 C. Battistoni, V. Di Castro and G. Mattogno, *Inorg. Chim. Acta, 22*, L15 (1977).
5 L. J. Matienzo and S. O. Grim, *Inorg. Nucl. Chem. Letters, 9*, 731 (1973).
6 a) QCPE Progr. 261, Chem. Dept. Indiana Univ., Bloomington, IN 47401;
b) R. M. Summerville and R. Hoffmann, *J. Am. Chem. Soc., 98*, 7240 (1976);
c) (MNDO program) M. J. Dewar and W. Thiel, *J. Am. Chem. Soc., 99*, 4899 (1977).
7 See *e.g.* 'Handbook of X-ray and UV–PE Spectroscopy', ed. D. Briggs, Heiden (London) 1977, ch. 2, p. 85.
8 R. Larsson, *J. El. Spectr., 24*, 57 (1981).
9 E. Borghi, C. Furlani and G. Mattogno, *J. Microsc. Spectr. El., 3*, 241 (1971).