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Electronic structure of thiaporphyrins: an X-ray photoelectron spectroscopic study †

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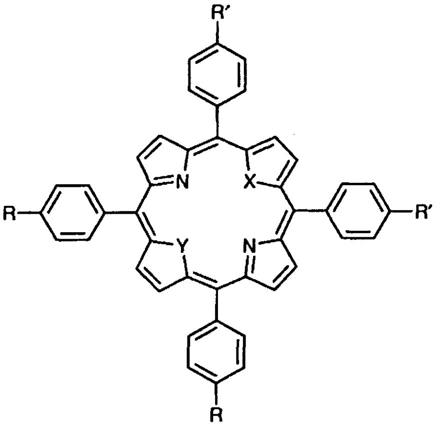
The electronic structure of 5,10,15,20-tetraphenylporphyrin ($\mathrm{H_2tpp}$) modified with one and two sulfur core atoms has been investigated by X-ray photoelectron spectroscopy (XPS). The nitrogen 1s binding energies (b.e.s) were excellent sensors of the electronic effects of the core-modified porphyrins. They clearly show that there is an increase in electron density on the core nitrogen atoms when the two NH groups in $\mathrm{H_2tpp}$ are replaced by sulfur atoms, the nitrogen 1s b.e. decreasing by about 1.5 eV. The carbon 1s core level also decreases in b.e. on core modification with sulfur atoms. The results obtained are in good agreement with those from UV/VIS, fluorescence spectroscopy, electrochemical studies, X-ray diffraction and extended-Hückel calculations. They indicate that there is an interaction between the nitrogen and sulfur atoms and a mechanism is suggested for it. No evidence was found for interaction among sulfur atoms and the participation of their d orbitals in the electronic structure. Copper and nickel complexes of the monothiaporphyrin were also subjected to XPS analysis.

A standard *modus operandi* for establishing the structure and bonding in any compound is the comparison of data derived from many spectroscopic techniques. To this end a good number of techniques have been applied to porphyrins and their core-modified derivatives, *e.g.* UV/VIS,[1] fluorescence,[2] NMR,[3] ESR,[4] X-ray diffraction[5] and electrochemical techniques.[4a,6] However X-ray photoelectron spectroscopy (XPS) has been applied only to a limited extent in the study of porphyrin electronic structure.[7] Its utility must be judged in the light of its sensitivity to changes in atomic charges and bonding parameters. A system enabling such an investigation is 5,10,15,20-tetraphenylporphyrin ($\mathrm{H_2tpp}$) and its derivatives modified with one and two core sulfur atoms.

With the help of photoemission techniques only, researchers ascertained the presence of two distinctly different, non-equivalent nitrogen types in the porphyrin free base[7] in the early seventies. These results eliminated the possibility of a bridged free-base structure as had been postulated earlier but which would require a single nitrogen 1s peak. Efforts have also been aimed at correlating the XPS results with charge densities calculated by molecular orbital (MO) theory. Qualitative correlations were recently found in the nitrogen 1s binding-energy shifts of $\mathrm{H_2tpp}$ and its derivatives by Gassman and co-workers.[8] However there is no report on the XPS studies of thiaporphyrins.



$\mathrm{H_2L^1}$ ($\mathrm{H_2tpp}$)	X = Y = NH; R = R′ = H
$\mathrm{HL^2}$	X = S; Y = NH; R = R′ = H
$\mathrm{HL^3}$	X = S; Y = NH; R = R′ = $\mathrm{OCH_3}$
$\mathrm{HL^4}$	X = S; Y = NH; R = OH; R′ = $\mathrm{CH_3}$
$\mathrm{L^5}$	X = Y = S; R = R′ = H
$\mathrm{L^6}$	X = Y = S; R = R′ = $\mathrm{OCH_3}$

When the two NH groups in $\mathrm{H_2tpp}$ ($\mathrm{H_2L^1}$) are each replaced by the Group 16 heteroatom sulfur the core size of the macrocylc is reduced[5b] due to larger size of the sulfur atoms and this may lead to significant bonding across the core of the porphyrin. It should be noted that the observed distances between the sulfur atoms is markedly shorter than the sum of the van der Waals radii.[9] However, the nuclear least-squares plane (n.l.s.p.) of $\mathrm{L^5}$ is more 'puckered' than that of its selenium analogue, though selenium is larger in size, and n.l.s.p. of the tetrathiaporphyrin dication is highly 'puckered'.[5a] Presuming that there are bonding interactions within the core between sulfur atoms the changes in the ^{1}H NMR chemical shifts and electrochemical results can be explained.[3,6] However, X-ray diffraction results[5b] do not favour the suggestion offered to explain the ^{1}H NMR results[3] of $\mathrm{L^5}$ in terms of changes in the inner and outer aromaticity produced by specific core interaction. Moreover iterative extended-Hückel (IEH) calculations on $\mathrm{L^5}$ with and without considering the participation of d orbitals of sulfur show the charge density on S to change only slightly by 0.005 e.[9] However, there is a great difference in charge density on nitrogen atom as is evident from IEH calculations with (−0.258 e) and without (−0.299 e) considering sulfur d orbitals. If there is a significant change in the electron density at nitrogen and carbon it should be reflected in the nitrogen 1s and carbon 1s binding energies b.e.s of thiaporphyrins relative to $\mathrm{H_2tpp}$. Moreover, it should change the energies of the highest occupied molecular orbital (HOMO) and of the lowest unoccupied molecular orbital (LUMO). It appears that all the physical and chemical properties of porphyrins are affected when sulfur atoms are introduced into the core and the issue of S • • • S interaction and

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† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J, Torr ≈ 133 Pa.

d-orbital participation in the electronic structure are not yet settled. Hence, we felt that XPS studies are necessary for a better understanding of the electronic structure of thiaporphyrins and their different physical and chemical properties. Therefore we present here XPS results of H_2L^1, HL^2 and L^5 and *para*-substituted thiaporphyrins.

Experimental

The porphyrins were prepared as described in ref. 1. The XPS measurements were made with a VG ESCALAB Mk II spectrometer equipped with non-monochromatised Mg-Kα X-ray radiation. The spectrometer system has been previously described.[10] The samples were prepared by evaporating chloroform solutions of the porphyrins onto the sample cup made of an alloy. A small piece of silver metal was placed in such a way that part of it was beneath the surface but mostly on the top of the evaporated material in order to measure the extent of charging due to the poor conducting nature of porphyrins. An energy of 20 eV was used to achieve a sufficiently good signal-to-noise ratio in a reasonable time. The compounds are highly stable at high vacuum of the order of 10^{-9} Torr and there was no evidence of X-ray-induced damage for the lengths of time necessary for spectral data acquisition. For a particular sample, the XPS peak positions (±0.1 eV) and shapes remained highly reproducible from one run to another. The b.e.s reported[7] for H_2tpp are in good agreement with our results indicating that the above method of preparation of samples for XPS analysis is acceptable and reproducible.

Results and Discussion

Nitrogen 1s core-level XPS results for H_2L^1, HL^2 and L^5 are shown in Fig. 1. In all cases investigated, including the *para* derivatives of thiaporphyrins, the spectral characteristics are similar to those of their parent compounds. The nitrogen 1s, sulfur 2p and carbon 1s core-level b.e.s of the porphyrins investigated are presented in Table 1. As shown in Fig. 1(*a*), two resolved peaks are observed in the N 1s spectra of H_2L^1 and a clean single N 1s peak is observed for L^5 [Fig. 1(*c*)]. However, for HL^2 the overlapping peaks were deconvoluted [Fig. 1(*b*)] with a computer program[11] developed in our laboratory.

Table 1 Binding energies (eV) of nitrogen 1s, carbon 1s and sulfur 2p core levels of H_2L^1 and thiaporphyrins

	Nitrogen 1s			
Compound	>N–H	=N–	Carbon 1s	Sulfur 2p
H_2L^1	400.1	398.0	284.3	—
HL^2	398.9	397.5	283.7	162.7
HL^3	398.9	397.5	283.6	162.7
HL^4	398.8	397.4	283.6	162.7
L^5	—	396.6	283.5	162.6
L^6	—	396.6	283.4	162.7

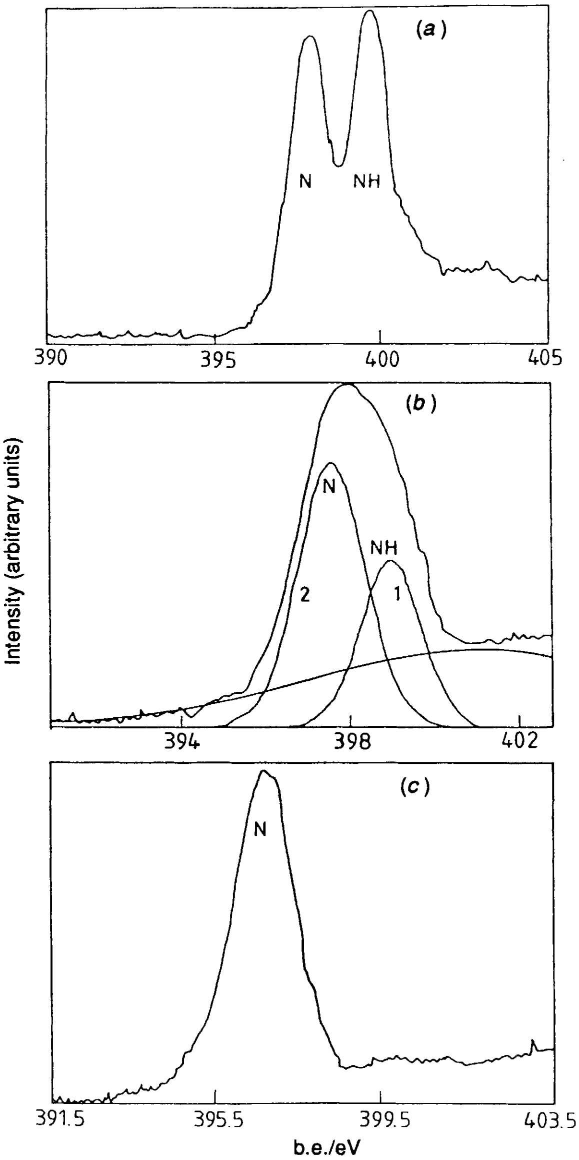

Fig. 1 Nitrogen 1s core-level spectra of (*a*) H_2L^1, (*b*) HL^2 and (*c*) L^5. Spectrum (*b*) is deconvoluted to show the presence of two types of nitrogen. A linear background subtraction was made

The =NH and ≡N nitrogens present in the H_2L^1 core had been assigned previously to the higher (400.1 eV) and lower (398.0 eV) b.e. peaks, respectively.[7,8] For HL^2 also the NH nitrogen appears at a higher b.e. (398.9 eV) compared to the ≡N nitrogens (397.5 eV). Both b.e.s are less than those of H_2L^1. In L^5 there is only one type of nitrogen, which appears at a b.e. of 396.6 eV. It is clear from the above results that the average electron density on the nitrogen atoms increases when S atoms are introduced into the porphyrin core by replacing NH groups.

The effect of replacing a NH group in H_2L^1 by one sulfur atom is a shift in b.e. to lower values for both types of nitrogens, but the effect is larger on the NH. On subsequent substitution by sulfur of one more NH group the b.e. of the ≡N nitrogens is lowered further. These shifts indicate the increase in electron density at the N atoms. This should destabilise the HOMO of L^5 as is reflected in the MO calculations of Gouterman and co-workers,[9] without considering the participation of sulfur d-orbitals. In L^5 and H_2L^1 the nitrogen p_x orbital continues to be the HOMO and the b_{3g} (π^*) orbital continues to be the LUMO.[9] As suggested above, the HOMO is destabilised on replacing NH groups by S atoms, leading to a decrease in the energy gap between the HOMO and LUMO. This is reflected in the red shift observed in UV/VIS, fluorescence spectra of HL^2 and L^5 relative to H_2L^1.[1,2] Moreover, the difference between the first oxidation potential and first reduction potential (Δ_{redox}), which corresponds to the HOMO – LUMO gap, is reduced.[6] This is in good agreement with our XPS results. If there is any participation of sulfur d orbitals in the electronic structure of L^5, as suggested by Ulman and co-workers[1,3,6] and Gouterman and co-workers,[9] it might reduce the electron density at N since the d orbitals will be populated depending on the extent of interaction between the sulfur atoms. However, our XPS results clearly reveal that there is a considerable increase in electron density at nitrogen. This is further supported by electrochemical results.

Besides nitrogen 1s spectra, carbon 1s core-level XPS results also provide interesting information. For all the thiaporphyrins reported here (Table 1), the carbon 1s b.e. is considerably lower than that of H_2L^1 and its *para*-substituted derivatives.[7,8] In general this indicates an overall increase in electron density on the carbon atoms of the macrocycle to different extents. We would like to point out the X-ray diffraction results on L^5 which indicate the puckered nature of the thiophene and pyrrole rings according to the dihedral angle between the plane of the four *meso* carbons and those of the four-membered rings.[5b] This may tilt the phenyl rings present outside the macrocycle in such a way as to increase the electron density on the C atoms of the macrocycle. In other words, there may be extended resonance interaction between the porphyrin carbon atoms and the phenyl rings. If this is true it will lead to a deshielding of the thiophene and pyrrole protons, which is observed experimentally.[3] However, the explanation given by Ulman *et al.*[3] in terms of the changes in inner and outer aromaticity produced by specific core interaction may not be correct. Apart from this the LUMO stabilisation is directly supported by the observation of increased electron density on the carbon atoms of L^5 and HL^2. Since the LUMO is mainly made up of antibonding orbitals of the carbon atoms, any increase in electron density on carbon brings the b_{3g} (π^*) and other π^* orbitals closer to the occupied orbitals. The first oxidation and reduction potentials of H_2L^1 (1.03, −1.23 V), HL^2 (1.08, −1.074 V) and L^5 (1.17, −0.94 V) respectively show a shift to more positive values,[1b,6] but the effect on the reduction process is much larger. This may be mainly attributed to the stabilisation of the LUMO as explained above.

It should be noted that different mechanisms are operative for the stabilisation of the LUMO and destabilisation of the HOMO. An increase in resonance interaction between the peripheral phenyl rings and the C atoms of the porphyrins stabilises the LUMO and results in the carbon 1s energy moving to lower b.e. On the other hand, the introduction of sulfur atoms, having higher van der Waals radii and lower electronegativity than those of nitrogen, can be expected to destabilise the filled orbitals by providing large electron densities.[12] This is observed in our XPS results. Ultimately it indicates that there is no participation of sulfur d orbitals in the electronic structure of thiaporphyrins. If there had been any the consequence would have been to reduce the electron density on nitrogen resulting in an increase in the b.e. of the nitrogen 1s core level. This is just the opposite of what we have observed.

The reduction of the HOMO − LUMO gap, which occurs on replacing NH groups by sulfur atoms, is explained by destabilisation of the HOMO and stabilisation of the LUMO, but the magnitudes of the two effects are different. This is reflected in the red shift observed in UV/VIS, fluorescence spectra of thiaporphyrins.[1,2] Moreover, our XPS results are in good agreement with the reduction in Δ_{redox} as we substitute NH groups by S atoms as evidenced by the reported values: H_2L^1, −2.26; HL^2, −2.15 V; and L^5, −2.10 V.[1b] There is a linear relationship between the nitrogen 1s b.e., Δ_{redox} and the Soret band (Fig. 2) positions.

The relationship is valid when the heteroatom bonding is not considered. We would like to point out the contradiction between our XPS results and reported electrochemical results.[6] The first oxidation potentials for H_2L^1 (1.03 V) and L^5 (1.17 V) suggest stabilisation of the HOMO, whereas our XPS results on the ≡N 1s b.e. of H_2L^1 (398.0 eV) and L^5 (396.6 eV) suggest destabilisation of the HOMO. The first reduction potentials for H_2L^1 (−1.23 V) and L^5 (−0.94 V) suggest stabilisation of the LUMO comprising carbon π orbitals. We feel that though the previous authors suggested stabilisation of the LUMO, the mechanism provided in terms of electron loss from the outer ring due to the S ··· S bonding interaction may not be correct. In fact such loss should destabilise the LUMO. The lower b.e. observed for the carbon 1s core level in L^5 (283.5 eV) compared to H_2L^1 (284.3 eV) is also in accord with stabilisation of the LUMO through the bonding interaction between the phenyl rings and the porphyrin macrocycle. Recent theoretical calculations by Takeuchi *et al.*[13] on halogenated porphyrins clearly demonstrate that the electronic effect due to the halogens is to stabilise both the HOMO and LUMO; however this stabilisation is counteracted by distortion of the macrocycle, which leads to a large destabilisation of the HOMO and a smaller destabilisation of the LUMO. In the absence of any ionic substituents on the porphyrin periphery, the second effect is predominant in our L^5 due to its puckered nature compared to H_2L^1. The above theoretical results[13] are in good agreement with our observation of higher electron density on nitrogen and hence destabilisation of the HOMO in L^5. However the extended resonance interaction between the porphyrin carbon atoms and the phenyl rings stabilises the LUMO as explained earlier. Hence the explanation provided from our XPS results effectively reduces the gap between the HOMO and LUMO, and we believe it is more consistent with other experimental and theoretical results. This probably indicates that there is no S ··· S interaction. There is an additional proof from the XPS of the sulfur atoms as discussed below.

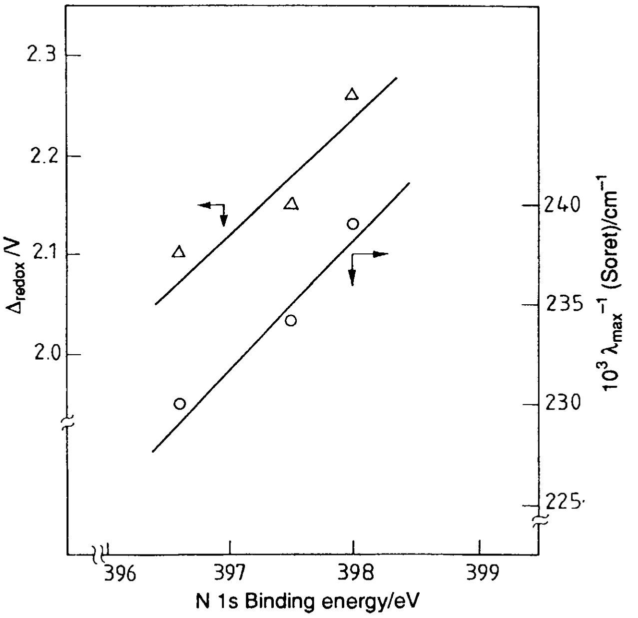

Fig. 2 Plots of the nitrogen 1s binding energy of H_2L^1 and thiaporphyrins against the difference between the first oxidation potential and first reduction potential (Δ_{redox}) and the Soret band energy

The sulfur 2p core level analysed for HL^2 and L^5 shows a single broad peak, due to a spin–orbit doublet, at about 162.6 eV. By comparison with b.e.s of standard compounds,[14] it is ascertained that sulfur forms a covalent bond with carbon atoms. The *para*-substituted thiaporphyrins do not show a shift more than ± 0.1 eV which is within the instrumental limit. This observation implies that the nature of the sulfur atoms is the same in HL^2 and L^5. If there is any S ··· S interaction it may have been manifested in XPS. However, the observation of the same b.e. for HL^2, L^5 and its *para* derivatives does not support the S ··· S interaction and hence any d-orbital participation in their electronic structures. The atomic charges calculated by Gouterman and co-workers[9] on L^5, without considering sulfur d-orbital participation, S (0.176) and N (−0.299), suggest that there may be charge localisation on nitrogen and sulfur. Our XPS results are in very good agreement with this. If there is really a negative charge localisation on nitrogen and a small positive charge localisation on sulfur, it may considerably reduce the inner-ring aromaticity in the thiaporphyrin core and eventually this may lead to π delocalisation on the outer ring of the porphyrin. It is worthwhile noting that Ulman *et al.*[3] came to the same conclusion on outer-ring aromaticity, though by a different rationale from the NMR results.

From X-ray diffraction results on HL^2 and L^5,[5b] it is clear that the adjacent S···N distance is about 3 Å, which is considerably shorter than the sum of the van der Waals radii for S and N (3.35 Å). This short distance may lead to a charge transfer from sulfur to nitrogen, which is further supported by the electronegativity difference between sulfur and nitrogen. This is probably the reason for the considerable difficulty in forming metallodithiaporphyrins. However, this charge-localisation hypothesis can be understood clearly from the XPS of metallothiaporphyrins, and provides some insight into their electronic structure.

We therefore carried out XPS measurements on $[CuL^2Cl]$ and $[NiL^2Cl]$. The b.e.s observed for the nitrogen 1s, carbon 1s, sulfur 2p, copper $2p_{\frac{3}{2}}$ and nickel $2p_{\frac{3}{2}}$ core levels are given in Table 2. Copper and nickel core-level spectra are shown in Fig. 3. The single peak observed for the nitrogen 1s core level in each case demonstrates that all the three nitrogen atoms are more or less equal in terms of electron density, and is consistent with ESR[4a] and X-ray diffraction,[15] results. Upon metal complex formation with Ni or Cu all the elements show an increase in b.e. compared with those of the free base HL^2. The higher b.e. observed for the S 2p levels of the complexes compared to that of the free base suggest that the porphyrin tends to reduce the metal. However, the b.e. for the metal core levels (932.8 and 852.7 eV, respectively) are lower than expected, *e.g.* 934.6 eV for [Cu(tpp)], 855.1 eV for [Ni(tpp)].[7e] This observation clearly supports and is consistent with our charge-localisation hypothesis. We attribute this mainly to the charge transfer from the ligand to the metal (l.m.c.t.) on complexation.

The large electron density localised on the nitrogen atoms in the free base HL^2 is stabilised by l.m.c.t. on complex formation with metal ions. Cyclic voltammetric results show that the first oxidation potential of $[CuL^2Cl]$ is higher than that of HL^2.[4a] The b.e. reported for the Cu $2p_{\frac{3}{2}}$ core level in $CuCl_2$ (934.6 eV)[16] and the Ni $2p_{\frac{3}{2}}$ core level in $NiCl_2$ (855.6 eV)[17] are higher than those of the corresponding $[ML^2Cl]$. This unambiguously shows that there is substantial l.m.c.t. Our XPS results also demonstrate the stabilisation of the nitrogen orbitals and corresponding increases in b.e. The lower b.e.s observed for the metal core levels of $[CuL^2Cl]$ and $[NiL^2Cl]$ indirectly support the XPS results for HL^2 and L^5.

We would like to point out that the solid-state effects and time-scale involved should be considered when analysing XPS and X-ray diffraction results. In solution studies solid-state effects are absent and the time-scale is high as for electrochemical and NMR techniques, and this may be a reason for the contradictory results observed in solution studies where the intermolecular forces are minimal.

Conclusion

The b.e.s of the nitrogen 1s and carbon 1s core levels clearly show that there is an increase in electron density on the core nitrogen and macrocylic carbon atoms respectively when the two NH groups in H_2L^1 are replaced by sulfur atoms. The large electron density on nitrogen and carbon respectively destabilise the HOMO and stabilise the LUMO. Based on XPS results, a new mechanism is proposed for the reduction in HOMO − LUMO energy gap between unsubstituted porphyrins and thiaporphyrins. We have indicated that there is an interaction between the N and S atoms and suggest a mechanism for it. However, we do not find any evidence for an interaction among the sulfur atoms and the participation of their d orbitals in the electronic structure. Charge localisations on nitrogen and sulfur atoms in thiaporphyrins are proposed. The XPS results for $[CuL^2Cl]$ and $[NiL^2Cl]$ provide support for the above concept and l.m.c.t.

Table 2 Metallothiaporphyrin binding energies (eV)

Compound	Nitrogen (1s)	Carbon (1s)	Sulfur (2p)	Metal ($2p_{\frac{3}{2}}$)
$[NiL^2Cl]$	398.8	284.7	163.6	852.7
$[CuL^2Cl]$	398.7	284.8	163.7	932.8

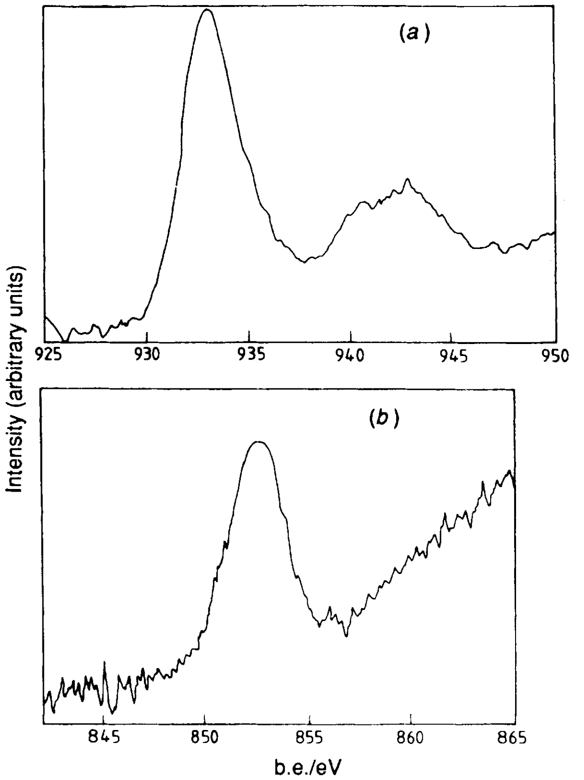

Fig. 3 (*a*) The Cu $2p_{\frac{3}{2}}$ spectrum of $[CuL^2Cl]$ and (*b*) the Ni $2p_{\frac{3}{2}}$ spectrum of $[NiL^2Cl]$

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