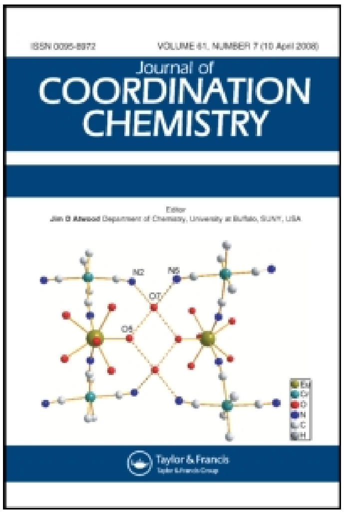

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AN X-RAY PHOTOELECTRON AND INFRARED SPECTROSCOPIC STUDY OF NICKEL SQUARATE DIHYDRATE AND BIS(2,4-PENTANEDIONATO)NICKEL(II)

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AN X-RAY PHOTOELECTRON AND INFRARED SPECTROSCOPIC STUDY OF NICKEL SQUARATE DIHYDRATE AND BIS(2,4-PENTANEDIONATO)NICKEL(II)

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The X-ray photoelectron spectra of nickel squarate dihydrate and of bis(2,4-pentanedionato)nickel(II) are interpreted in terms of the known crystal structures of these complexes. The comparative degree of pi-electron delocalisation over metal and ligand for these complexes is also evaluated from the XPS data.

INTRODUCTION

Bis(2,4-pentanedionato)nickel(II) and nickel(II) squarate both contain oxygen donor bidentate ligands and chelate ring systems stabilized by extensive electron delocalisation. Electron delocalisation in bis(2,4-pentanedionato)nickel(II) is a consequence of the metal complexing with the enol form of the ligand and

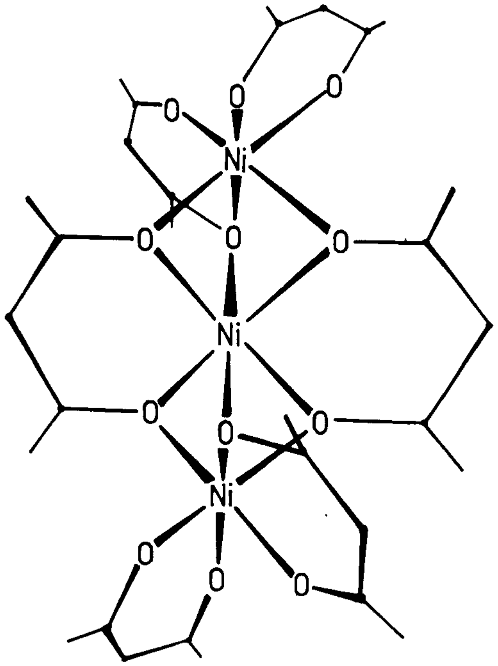


FIGURE 1 The structure of bis(2,4-pentanedionato)nickel(II).[3]

[†]Author for correspondence.

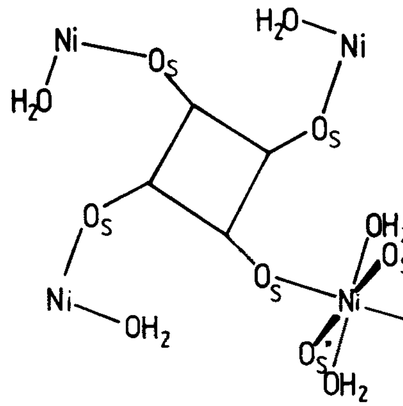
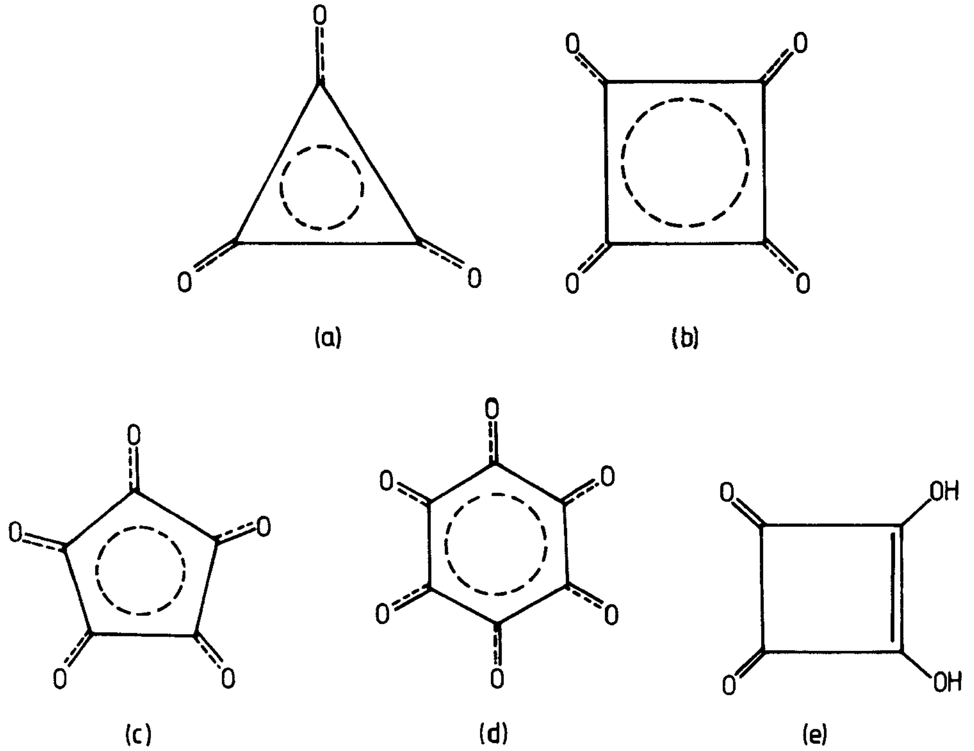


FIGURE 2 The structure of nickel squarate dihydrate[6,7] showing the bonding of one squarate ion to four different nickel ions within a twinned structure. (O_s defines squarate oxygens; O_s' and O_s'' indicate different squarate oxygens coordinated to one Ni(II) ion).

electron delocalisation in nickel(II) squarate results from an interaction of the metal with the π-system of the squarate anion.

The structures of these complexes are not simple. Bis(2,4-pentanedionato)nickel(II) is trimeric in the solid state (Fig. 1)[1-5] and nickel(II) squarate is a pseudo-trimeric structure comprising three $NiC_4O_4.2H_2O$ molecular units per unit cell (Fig. 2).[6-7]



(a) (b)

(c) (d) (e)

FIGURE 3 (a): Deltate anion $C_3O_3^{2-}$; (b): Squarate anion $C_4O_4^{2-}$; (c): Croconate anion $C_5O_5^{2-}$; (d): Rhodizinate anion $C_6O_6^{2-}$; (e): Squaric acid (diketocyclobutenediol).

For the present study, it is relevant and advantageous to consider the squarate anion in conjunction with other known cyclic pseudo aromatic anions of the series $C_nO_n^{2-}$ [7-9] namely deltate $(C_3O_3)^{2-}$,[10] croconate $(C_5H_5)^{2-}$ [11-15] and rhodizinate $(C_6H_6)^{2-}$,[8] (Fig. 3). Squaric acid (diketocyclobutanediol) is also the precursor of many cyclic compounds of general interest[9,16-23] such as deltic acid;[14] hence a structural study of the metal complexes of one member of the $C_nO_n^{2-}$ series provides a valuable insight into the chemistry of the series as a whole.

Some theoretical calculations on $C_nO_n^{2-}$ anions which are relevant to the present study have been reported. For example, Habenschuss and Gerstein[7] have reported that the delocalised π-system of the squarate anion has a van der Waals' thickness of approximately 0.34 nm, which is similar to that of many aromatic compounds. It has also been shown that as the anionic ring size in $(C_nO_n)^{2-}$ increases, the total delocalisation energy increases,[24] while the delocalisation energy per atom in the ring decreases. Further, LCAO-MO calculations of West and Powell[25] for the squarate anion, indicate oxygen and carbon charges of $q_O = -0.736$ and $q_C = +0.236$ with π-bond orders of (C-C) = 0.471 and (O-C) = 0.542.

Tolman *et al.*[26] have applied XPS to study the nickel, oxygen and carbon environments in $[Ni(acac)_2]_3$ with no mention of the satellite spectra, while nickel squarate has not been studied previously using XPS. The present XPS study provides a comparative analysis of $Ni2p_{3/2}$ and $Ni2p_{1/2}$ core level binding energies for these two complexes together with analysis of their satellite spectra. The Ni2p core level photoelectron satellite spectra are interpreted in terms of the degree of covalency[26] of the respective metal-oxygen coordinate bonds. The overall XPS data are interpreted with respect to the known structures of these complexes.

The present XPS study of nickel squarate also forms a basis for a similar study of a range of structurally related complexes formed *via* partial or complete replacement of the squarate carbonyl oxygens by sulphur,[17,18] selenium,[19] dicyanomethylene[20-22] and nitrogen.[16]

EXPERIMENTAL

XPS spectra were recorded on a spectrometer previously described by Kemeny *et al.*,[27] using MgKα photons of energy 1253.6eV. Powder samples were pressed into homogeneous discs (~13 mm diameter, 2 mm thickness) and affixed to a double-sided copper sample holder. The metal $Cu2p_{3/2}$ electron binding energy (932.50eV)[28] served as a calibrant level for all core level binding energies relative to the spectrometer Fermi level. This copper peak was measured for a scraped (in air) and partially passivated surface.

The binding energies referenced in this way are then subsequently quoted with error ±0.3eV. The spectrometer vacuum pressure was $10^{-6} \rightarrow 10^{-7}$ hPa (≈torr). Since the samples are non-conducting, a check was made for surface charging effects which may cause a 'floating' Fermi level. This was done by varying the intensity of the X-ray source (50→300 W, Leybold-Heraeus RQ10/63). The copper sample holder and sample were situated inside a cylindrical metal housing section of the spectrometer. The MgKα X-rays entered through a slot in the side of the cylinder while the photo-electrons passed through a fine slit in the cylinder prior to entering the electron energy analyser. No surface charging effects were observed with variation in X-ray intensity, which suggests that the generation of secondary electrons inside the housing was sufficient to act as a 'flood gun' for the sample surface. As a result, no binding energy corrections were necessary.

Infrared spectra were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer over the range 4000-250 cm^{-1}, using the KBr pellet method. All IR bands were calibrated relative to polystyrene. Elemental analyses were provided by the Australian Microanalytical Service, Melbourne, Australia.

Nickel(II) squarate dehydrate was prepared according to the procedure of Gerstein and Habenschuss.[6] Anal.; Calcd. for $NiC_4O_4.2H_2O$: C, 23.23; H, 1.94; O, 46.4%. Found: C, 23.40; H, 4.19; O, 45.9%. Infrared spectrum (main bands): 1585s (C-O str), 1462 (C$\overline{\cdots}$C str), 1230s, 1220s (C$\overline{\cdots}$O str), 1135s (O-H def), 1095s (C-C str), 985s, 950s (C=C def, out of plane), 772s ($Ni-OH_2$ rock), 670s, 662s, (Ni-O rock), 540s ($Ni-OH_2$ wag) and 450s (Ni-O str). The assignment for $\bar{\nu}$(C-C str) is in good agreement with that of Ito and West;[29] however they report the $\bar{\nu}_{12}$(C-O str) vibration at 1530 cm^{-1} (sb) with additional bands at 350 m (C-O def, in plane) and 259s (C-O def, out of plane).

Bis(2,4-pentanedionato)nickel(II) was synthesised by Cavell *et al.*[30] Anal.; Calcd. for $Ni(C_5H_7O_2)_2$: C, 46.8; H, 5.5%. Found: C, 47.0; H, 5.4%. Infrared spectrum (main bands): 1585sb (C=C str), 1500sb (C=O str), 1410sb (C-H def), 1254s (C-O str), 1190s (C-C str, C-Me), 1013s (C-C str, acac), 920s (C=C def, out of plane), 765s (C-H rock), 655s (Ni-O rock), 580s (Ni-O wag) and 425s (Ni-O str). This spectrum is consistent with that reported by Nakamoto *et al.*[31] and Fackler *et al.*[32]

RESULTS AND DISCUSSION

Prior to discussion of the XPS data, it is necessary to summarise the essential features of the X-ray crystallographic data for these complexes.

For $[Ni(acac)_2]_3$, Bullen *et al.*[3,4] have shown that each of the three nickel atoms of the trimeric unit is essentially in a distorted octahedral environment of oxygen atoms and that pseudo-centrosymmetry is exhibited as a result of a linear orientation of the three constituent nickel atoms. The overall structure may be viewed as a combination of three octahedra with sharing of triangular faces. Thus the three nickel atoms are in two different NiO_6 environments resulting from two octahedra sharing one triangular face and one central octahedron sharing two triangular faces. The non-equivalent nickel centres are reflected in the Ni-O bond lengths. The Ni-O bond length is 2.01 Å when monodentate oxygen is involved and 2.12 Å when bridging oxygen is involved.

For $NiC_4O_4.2H_2O$, Habenschuss and Gerstein[7] have confirmed an overall octahedral structure involving nickel coordinated to four squarate type oxygens and two water of hydration oxygens. The squarate ions form a macroscopically twinned structure with each squarate oxygen bonded to a different nickel atom. Such twinning creates a 4.7 Å wide void within the unit cell which is filled by a clathrated water molecule.[6,7] Also, each axially bound water molecule is hydrogen-bonded to different squarate oxygens. Overall, it is not possible to differentiate between the various types of bound oxygen in the structure and hence the constituent nickel atoms are in essentially equivalent environments.

The XPS data obtained for bis(2,4-pentanedionato)nickel(II) and nickel(II) squarate dihydrate are recorded in Table I, together with other reported XPS data: (*i*) $[Ni(acac)_2]_3$,[26] (*ii*) a trifluoroacetylacetonate complex of nickel(II)[33] and (*iii*) bis(acetato)nickel(II) tetrahydrate[33] for comparative purposes.

As a preamble to detailed analysis of the XPS spectra of $[Ni(acac)]_3$ and $NiC_4O_4.2H_2O$, the presence of satellites in the $Ni(2p_{3/2,1/2})$ spectra is consistent with the paramagentism[33] of these complexes and the octahedral environment of coordinated nickel.

The structure of $[Ni(acac)_2]_3$ indicates two different oxygen environments within the molecular unit resulting from six shared β-ketoenolate oxygens associated with the central nickel ion of the trimer and six non-shared β-ketoenolate oxygens associated with the terminal nickel ions. However, the single broad E_b O(1s) peak at 530.8 eV for this complex is consistent with one oxygen environment and possibly results from

TABLE I
XPS binding energies of $NiC_4O_4.2H_2O$, $[Ni(acac)_2]_3$ and related complexes

Ni(II) complexes	$Ni2p_{3/2}$ (a) (eV)	$Ni2p_{3/2}$ (b) (eV)	$Ni2p_{1/2}$ (a) (eV)	$Ni2p_{1/2}$ (b) (eV)	O1s (eV)	C1s (eV)	$Ni2p_{3/2}$ [(b)-(a)](eV)	$Ni2p_{1/2}$ [(b)-(a)](eV)
$[Ni(acac)_2]_3$	856.9	861.6	874.0	880.8	530.8		4.7	6.8
$NiC_4O_4.2H_2O$	857.9	862.6	875.9	880.7	532.2		4.7	4.8
"Ni(tfac)" [33]	854.3	858.3	871.8	880.6			4.0	8.8
$Ni(OAc)_2.4H_2O$[33]	855.5	860.0 863.5	872.9	878.8			4.6 8.0	5.9
$[Ni(acac)_2]_3$[26]	856.1				532.0	285.0 286.4 (sh)		

(a) Main core level binding energy (±0.3 eV); (b) Satellite binding energy (±0.3 eV); [(b)-(a)] = "shake-up" transition energy (±0.6 eV); sh = shoulder.

pi-electron delocalisation within the acetylacetonate ring effectively equalizing the net charges on all oxygen atoms. Furthermore, the X-ray crystallographic data for this complex infer two different nickel ion environments which should be reflected as two $Ni(2p_{3/2})$ peaks with an intensity ratio of 2:1.

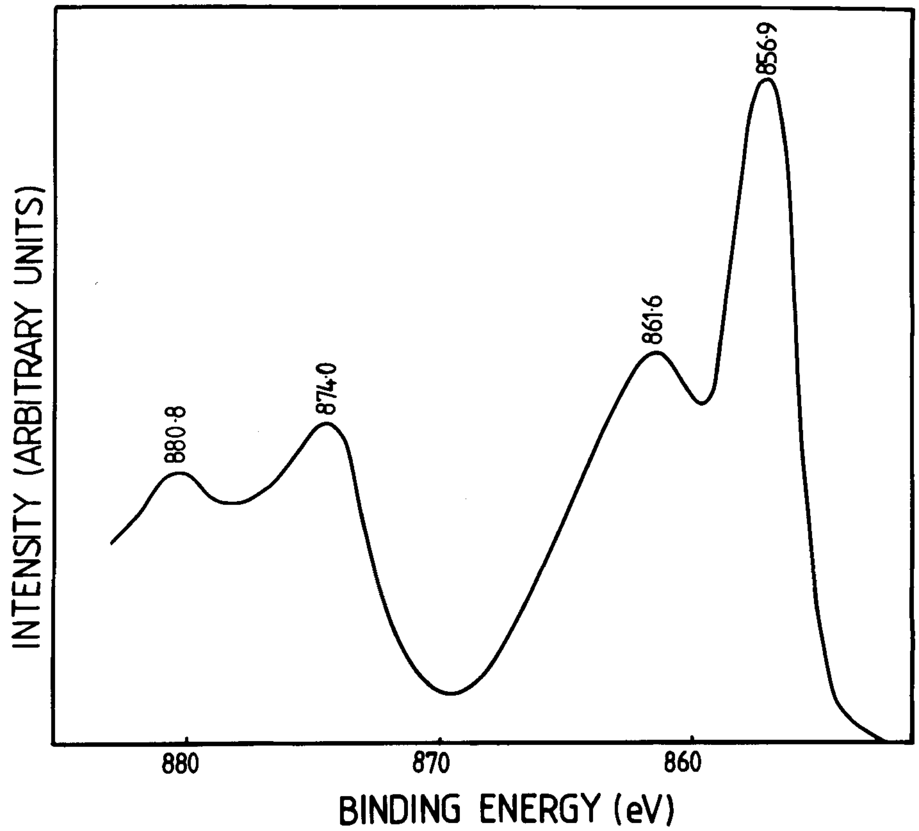


FIGURE 4 The $Ni2p_{3/2,1/2}$ XPS Spectrum of $[Ni(acac)_2]_3$, with associated shake-up satellites.

The $Ni(2p_{3/2,1/2})$ XPS spectrum of $[Ni(acac)_2]_3$ is shown in Fig. 4. Four peaks are evident at 856.9, 861.6, 874.0 and 880.8 eV respectively. It is immediately apparent that the two different nickel environments are not resolved. The peaks may be assigned as $E_b(Ni2p_{3/2})$, $E_b(Ni2p_{3/2})$ satellite, $E_b(Ni2p_{1/2})$ and $E_b(Ni2p_{1/2})$ satellite, respectively. Hence, it is concluded that the electronic environment of, or alternatively the charges on, the constituent nickel atoms of the molecular unit are essentially equivalent, due to extensive pi-electron delocalisation over metal and ligand.

The X-ray crystallographic data for $NiC_4O_4.2H_2O$[6,7] suggest one site type for the constituent nickel atoms of the molecular unit and two oxygen site types. The $Ni(2p_{3/2,1/2})$ XPS spectrum for this complex, as shown in Fig. 5, is consistent with one nickel electronic environment. Four peaks are evident at 857.9, 862.6, 875.9 and 880.7 eV respectively which may be assigned sequentially as $E_b(Ni2p_{3/2})$, $E_b(Ni2p_{3/2})$ satellite, $E_b(Ni2p_{1/2})$ and $E_b(Ni2p_{1/2})$ satellite. The O(1s) spectrum for this complex (Table I) consists of one broad unresolved peak at 532.2 eV. Hence it is not possible by XPS to differentiate between the two oxygen site types inherent in the structure of this complex.

In order to compare the binding energy data for these two complexes, it is necessary to discuss the factors which affect XPS chemical shifts. XPS chemical shifts or binding energy shifts may be expressed as in the following equation:[34-36]

$$\Delta E_b(m) = K_m q_m + \sum_{l \neq m} \left[\frac{K_l q_l}{r_{lm}} \right] - R^{ea} \qquad (1)$$

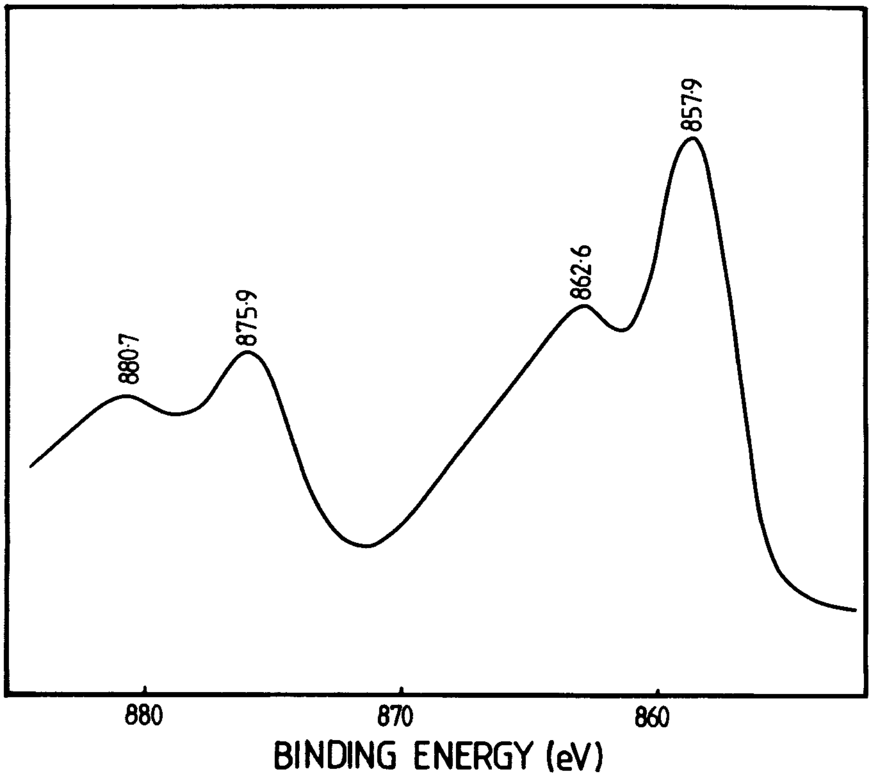


FIGURE 5 The $Ni2p_{3/2,1/2}$ XPS Spectrum of $NiC_4O_4.2H_2O$, with associated shake-up satellites.

$\Delta E_b(m)$ is the binding energy shift of a bound atom relative to that of a free atom m, K_m and K_l are constants, q_m is the charge on atom m under photoelectron study, q_l is the charge on the ligand atoms bonded to m, R^{ea} is the extra-atomic relaxation energy involved with photoemission from atom m and r_{lm} is the bond length between l and m. The term $\Sigma/l \neq m\ [K_l q_l/r_{lm}]$ is the interatomic effective potential, or molecular potential, which accounts for the potential on m from the ligating atoms (l) and the rest of the molecule. The terms K_m, K_l, r_{lm} and R^{ea} are taken to be effectively constant for the two complexes studied and hence the binding energy shift of the photoionised level of interest may be directly related to the charges q_m and q_l.

The larger Ni($2p_{3/2}$), Ni($2p_{1/2}$) and related satellites for $NiC_2O_4.2H_2O$ compared to $[Ni(acac)_2]_3$ reflect a lower electron density on nickel in nickel squarate dihydrate thereby inferring a greater degree of confinement of pi-electron density within the squarate ligand compared to the acac ligand. The approximate equivalence of 'shake-up' transition energy as related to the Ni($2p_{3/2}$) level (Table I) for the two complexes suggests an approximate equivalence in Ni-O bonding character in these complexes and therefore suggests a strong similarity of the metal electronic environments.

A further comparison of Ni-O bonding character in these complexes may be made using infrared data. For nickel squarate dihydrate, the Ni-O stretching and rocking modes are at 450 and 670, 662 cm^{-1}, respectively, whereas for $[Ni(acac)_2]_3$ the corresponding bands are at 425 and 655 cm^{-1}, respectively. These data suggest a slightly greater Ni-O bond order for nickel squarate dihydrate. Furthermore, from a comparison of XPS and infrared data for these two complexes, it is apparent that a greater charge differential exists between the nickel and donor oxygen atoms in nickel squarate dihydrate compared to $[Ni(acac)_2]_3$.

The overall lower binding energies for $[Ni(acac)_2]_3$ relative to those for $NiC_4O_4.2H_2O$ (Table I) reflects a greater electron density on nickel and donor oxygen in $[Ni(acac)_2]_3$ which decreases the effective nuclear charges q_m and q_l and indicates extensive pi electron delocalisation over metal and ligand which in turn reduces the charge differential between metal and donor oxygen in the latter complex.

It is relevant to comment that the 'shake-up' transition energies observed for these complexes fall within the range reported by Kim[37] and are consistent with a ligand-metal $\sigma_{eg}{}^{bo} \rightarrow 3d_{eg}{}^{ao}$ transition. The small differences in the Ni($2p_{3/2}$) binding enegy data of this study and those reported by Tolman *et al.*[26] may be due to differences in referencing procedures. Also the C(1s) binding energy data of Tolman *et al.*[26] for $[Ni(acac)_2]_3$ as shown in Table I are of little relevance to structural features. The main peak at 285.0 eV is assigned[26] to the methyl and methylene carbon atoms and the shoulder peak at 286.4 eV is assigned to the carbonyl carbon atoms of the ligand.

It is also of interest to interpret the XPS data for two other nickel(II) complexes as reported by Matienzo *et al.*[33] and given in Table I. It appears that the data for the trifluoroacetylacetonate complex of nickel(II) refer to the complex di-μ-aquo-di-μ_3-hydroxo-deca-(1,1,1-trifluoropentane-2,4-dionato) hexanickel(II) of stoichiometry $Ni_6(tfac)_{10}(OH)_2(H_2O)_2$. The structure of this complex has been reported by Cotton and Winquist[38] and consists of two trinuclear units joined by two bridging water molecules. Each nickel atom in the trinuclear unit is octahedrally coordinated to oxygen donor atoms of the tfac ligands, and such octahedral sub-units share a common vertex occupied by an hydroxide ion which bridges three nickel atoms. The large decrease in binding energies of the Ni(2p) levels (except the Ni($2p_{1/2}$) satellite) of the nickel tfac complex relative to those of $[Ni(acac)_2]_3$ is indicative of the strong electron withdrawing (-I) inductive effect of the terminal fluorine atoms of the tfac ligands, which increases the negative charge on the oxygen atoms (q_l), and therefore decreases the Ni($2p_{3/2,1/2}$) binding energies.

A similar explanation applies to the XPS data for $Ni(OAc)_2.4H_2O$. Relatively low

Ni(2p) core level binding energies are noted which reflect the electron withdrawing (-I) inductive effect of the ligand acetyl groups.

CONCLUSION

XPS data for bis(2,4-pentanedionato)nickel(II) and nickel squarate dihydrate are consistent with one type of metal and donor oxygen electronic environment for each complex which is explained on the basis of extensive pi-electron delocalisation within the respective molecular units. However, the XPS data further indicate that such electron delocalisation is greater for $[Ni(acac)_2]_3$ compared to nickel squarate.

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