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# X-Ray Photoelectron Spectra of Isonitroso(β-ketoimine) Complexes: Linkage Isomerism and Substituent Effects

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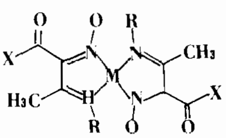
Isonitroso-β-ketoimines and isonitroso-β-imino esters contain several potential donor functions, and are known to act as ligands towards metals such as Ni(II) and Pd(II), either through imine nitrogen and isonitroso nitrogen, or through imine nitrogen and isonitroso oxygen. The former bonding mode (N,N) occurs alone in symmetric 1:2 chelates with Pd(II) (I) for isonitroso imino derivatives of acetoacetates [1] or N-alkylsubstituted acetylacetonates [2, 3], the latter (N, O) occurs (together with N,N) in asymmetric linkage isomers of type (II) which are present normally in Ni(II) complexes [4] and in Pd(II) complexes with N-unsubstituted imines of isonitrosoacetylacetonates [2] and can furthermore be formed for Pd(II) isonitrosoacetoacetatimines on isomerization of type (I) compounds [5]. Such chelating behaviour has been previously characterized in literature by i.r., pmr, and in some cases X-ray diffraction techniques [6–11]. The XPS techniques of investigation, whose data depend on atomic charge distributions and donor effects, appear particularly well suitable for elucidation of structural problems of this kind, and has been actually already preliminarily employed to support in some isolated cases the above structural assignments [1, 4, 7, 9, 11, 12].



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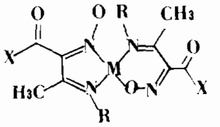

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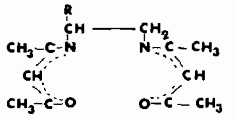
In the present work we report the results of a more extensive investigation of metal complexes of isonitroso(β-ketoimine) ligands, which allow a systematic characterization of their bonding mode, as well as of the effect of substituent groups on imino nitrogens, in particular the easy distinguishability of iminic- and isonitroso-nitrogen atoms on the ground of their XPS signals, and the possibility of distinguishing N,N from N,O coordination on the ground of XPS data.

X-ray photoelectron spectra were taken on a VG ESCA-3 spectrometer equipped with $AlK_{\alpha 1,2}$ source (1486.6 eV), according to the usual technique [13]. Measured b.e.s include C1s, N1s, O1s and Ni2p or Pd3d doublets. All values are referred to the contaminating carbon C1s signal taken as 285.0 eV; the actual C1s band contains several overlapping components, due essentially to alkyl C, alkoxy C, phenyl C from contamination, and carbonyl C, in order of increasing b.e.

Pd(II) complexes occur normally in the symmetric structure (I), containing two sets of inequivalent N atoms. Accordingly in compounds 1, 2 and 3 the N1s ionization region shows two distinct peaks, 2–2.5 eV far apart, assigned to imine nitrogen (398.4–399.2 eV) and to the isonitroso nitrogen, for which a higher b.e. is expected owing to the effect of the oxygen neighbour, around 401.1 eV. Each of the component bands has a FWHM of 2.0 eV, which, under our experimental conditions, corresponds to a single ionized species (*e.g.* 399.1 eV in 8 and 9, containing only one set of equivalent nitrogens). Presence of an alkyl substituent on imino nitrogen causes an increase of N1s b.e. of slightly less than 1 eV with respect to –NH, as already reported on other nitrogen compounds [14–17]; thus, N1s is 398.4–398.6 eV in the –NH compounds 1 and 2, and increases to 399.1–399.2 eV in the N-alkylsubstituted compounds 3, 4, 5, 6, 8 and 9. Pd $3d_{5/2}$ b.e. values fall in the normal range for planar Pd(II) complexes; a slight difference between 1 and 2 at 337.9 eV and 8, 9 at 337.4 eV can be ascribed to the effect of the $\underline{N}$–O donor in the chromophore; the same difference occurs *e.g.* between $[Pd(NH_3)_4]^{2+}$ or $[Pd(Oac)_2]$ (chromophore $[PdN_4]$ or $[PdO_4]$) reported at 338.5 in ref. [18]), and $[Pd(NH_3)_2(NO_2)_2]$ (chromophore $[PdN_2(\underline{N}-O)_2]$) at 339.0 in ref. [18].

Whereas compounds like 1, 2 and 3 appear stable, and their p.e. spectra do not change at all with time, in some other cases (4, 5, 6) a spontaneous transformation appears to occur even at room temperature after prolonged time and the final product exhibits different p.e. spectral patterns in the N1s region. In fact, the p.e. band in the N1s region in the spectra of 4, 5, 6 reported in Table I and Fig. 1 consists, after deconvolution, of three components in ratio 2:1:1 at 399.4, 400.1 and 401.3 eV respectively, which we assign in order of increasing b.e. to iminic nitrogens (at higher b.e. than in 1 or 2 because of the $-CH_3$ substituent), to an O-bonded isonitroso group, where N is less positive since it does not act as a donor towards Pd, and to the N-bonded isonitroso group, as in all previous cases; these patterns are consistent with an asymmetric bonding mode of type (II) [1]. Such structural assignment is further supported by comparison with the nickel complex 7. In fact, the

TABLE I. Binding Energy Values (eV) of Pd and Ni Compounds.

| $\mathrm{MeL_2}$ | | $\mathrm{L{:}\ X{-}\underset{O}{\underset{\|}{C}}{-}\underset{NO}{\underset{\|}{C}}{-}\underset{NR}{\underset{\|}{C}}{-}CH_3}$ | | | | |
|---|---|---|---|---|---|---|
| X | R | Pd 3d5/2 | Ni 2p3/2 | –N–R | –N–O–Me | –N–O |
| 1) $-OCH_3$ | H | 337.9 | — | 398.4 | — | 401.0 |
| 2) $-OC_2H_5$ | H | 337.9 | — | 398.6 | — | 401.1 |
| 3) $-C_6H_5$ | $C_3H_7$ | 338.0 | — | 399.2 | — | 401.2 |
| 4) $-OCH_3$ | $CH_3$ | 338.0 | — | 399.4 | 400.1 | 401.3 |
| 5) $-OC_2H_5$ | $CH_3$ | 338.0 | — | 399.4 | 400.1 | 401.2 |
| 6) $-OC_2H_5$ | $C_3H_7$ | 338.0 | — | 399.3 | 400.2 | 401.2 |
| 7) $-OCH_3$ | H | — | 854.8 | 398.5 | 400.5 | 401.2 |
| Pd L' | L' : |  | | | | |
| 8) | H | 337.4 | | 399.1 | | |
| 9) | $CH_3$ | 337.4 | | 399.1 | | |

nickel compounds are invariably assigned to an asymmetric structure (II) [4, 6, 12] and the N1s signal of 7 contains accordingly three components 2:1:1 attributed, in sequence, to the two iminic nitrogens at 398.5 eV (close to the =NH case in the palladium compounds 1 and 2), and to the O-bonded and N-bonded isonitroso nitrogens at 400.5 and 401.3 eV respectively, *i.e.* at b.e. values close to the analogous asymmetric Pd cases 4, 5 and 6. The envelope of the composite N1s band is different from that of the asymmetric compounds 4, 5 and 6 because of slight variations in the distance between components strongly affecting the superposition patterns: in 7, the N1s b.e. difference between the two types of isonitroso groups is smaller, and the b.e. of imino nitrogen in 7 is further apart from the isonitroso N1s b.e. values because of the presence of H rather than alkyl substituents. The Ni $2p_{3/2}$ value of 854.8 eV is in agreement with the usual findings for square planar Ni(II) [19, 20]. XPS data provide thus a valuable aid to the characterization of different bonding modes in isonitroso(β-dicarbonyl)iminato compounds.

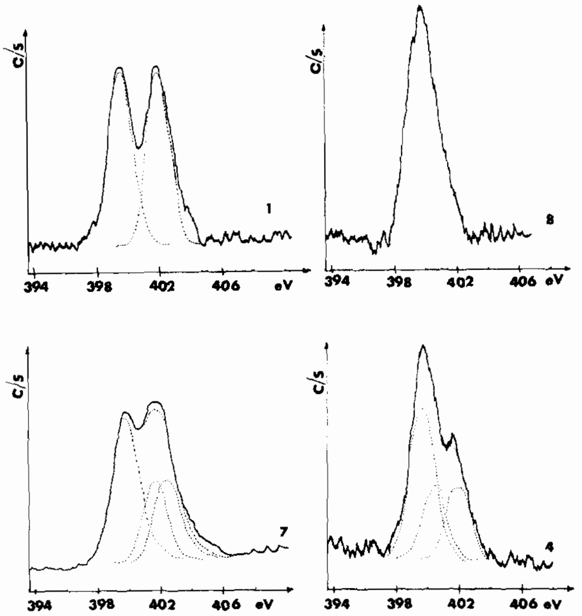


Fig. 1. Photoelectron N1s spectra of some Pd and Ni compounds.

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