Inorganica Chimica Acta, 31 (1978) L377–L378
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A Study of The Metal–Metal Bond in $Fe_2(CO)_6$-tBuNS and in $Fe_3(CO)_9S_2$ by means of Ultraviolet Photoelectron Spectroscopy

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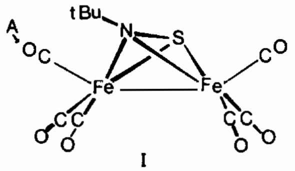
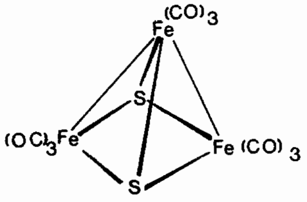
Received July 20, 1978

A large number of di- and trinuclear iron(0) complexes has been reported in the literature with bridging ligands ranging from sulphur atoms to large organic molecules [1, 2]. Although M.O. calculations for some of the binuclear complexes $Fe_2(CO)_6L$ have appeared in the literature the question whether the metal–metal bond is bent or straight has remained unsettled since no experimental evidence was known about the ordering of the orbital levels.

In this letter we present the UV photoelectron spectra (He(I) and He(II)) of $Fe_2(CO)_6$tBuNS (I) and $Fe_3(CO)_9S_2$ (II) in which metal–metal bonds are present (Figs. 1, 2). In both complexes the metal–metal distances are ~2.5 Å indicating single bonds [3].



I



II

The spectra of (I) show a band at 8.36 eV with a distinct shoulder at ~7.8 eV. He(I)/He(II) intensity differences clearly indicate that this band originates from iron d-electrons. Comparison with the M.O. calculations performed by Teo *et al.* [4] *via* the Fenske–Hall scheme for an analogous complex, $Fe_2(CO)_6S_2$, gives a very good agreement between the calculated and the observed bands for the d-orbitals. The calculations indicate that the metal–metal bond will be present at approx. 8.5 eV and that the remaining d-electrons are in accidently degenerate orbitals at a higher binding energy.

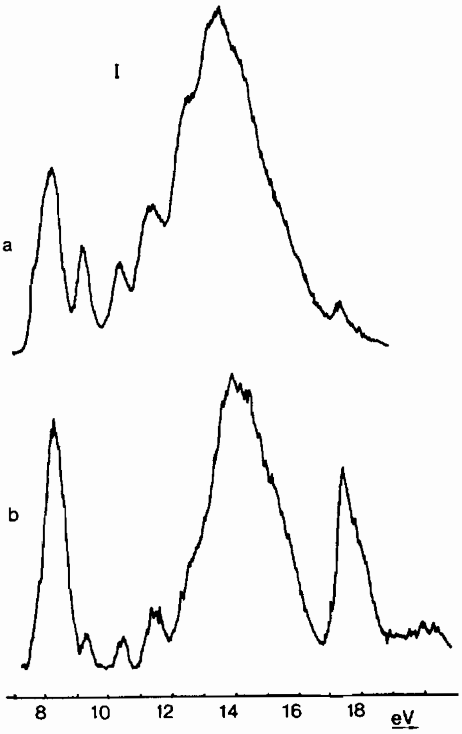


Figure 1. He(I) (a) and He(II) (b) photoelectron spectra of $Fe_2(CO)_6$tBuNS (I).

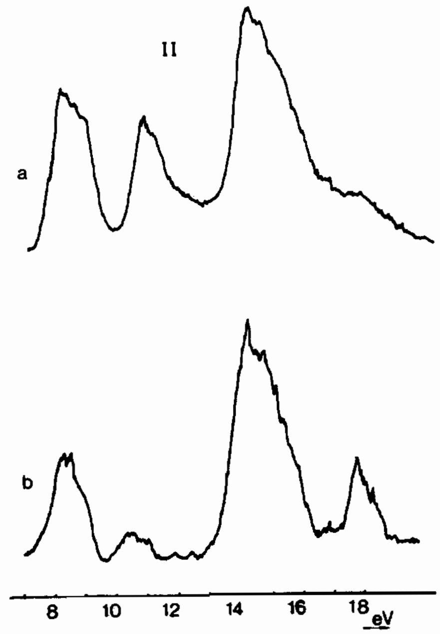


Figure 2. He(I) (a) and He(II) (b) photoelectron spectra of $Fe_3(CO)_9S_2$ (II).

It is also indicated that the carbonyl group (A) has a directing effect on the metal–metal bond and thus causes a bent metal–metal bond.

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In agreement with these calculations we assign the shoulder to the a^1 bent metal–metal bond and the sharp band at ~8.4 eV to the remaining d-electrons. The assignment of the remaining bands which are originating from the ligand is straightforward from He(I)/He(II) intensity differences and in agreement with CNDO-calculations [6].

In II two metal–metal bonds are present according to the crystal structure [5]. There are two six-coordinated and one seven-coordinated iron atoms. The P.E. spectra show a band at 8.35 eV with a shoulder again at approx. 7.8 eV and two shoulders on the high energy side. Based on intensity considerations and an extended Hückel type calculation [6] the latter shoulders are attributed to the d-electrons of the seven-coordinated iron. The more intense peak is assigned to the d-electrons of the six-coordinated iron atoms and the shoulder at 7.8 eV is again assigned to the metal–metal bond.

This indicates that the metal–metal bond is of the same nature and that the symmetry around the six-coordinated irons is essentially the same in both complexes.

The sulphur atoms are σ bonded to the iron atoms. The band at ~12 eV is assigned to the sulphur iron bonds on the basis of He(I)/He(II) intensity differences and on the extended Hückel calculations. The decrease in intensity on going from He(I) to He(II) radiation indicates that these electrons have predominant sulphur *p* character.

The results for I show the very good agreement with the Fenske–Hall calculation and thus give support for the bent bond description of the Fe–Fe bond. The metal–metal bond can be detected very easily with U.P.S. and comparison with the results for $Fe_3(CO)_9S_2$ shows clearly that the metal–metal bonds are of the same nature in both complexes.

Acknowledgment

Dr. R. Meij is thankfully acknowledged for providing us with the compounds.

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