On the State of Dinitrogen bound to Rhenium

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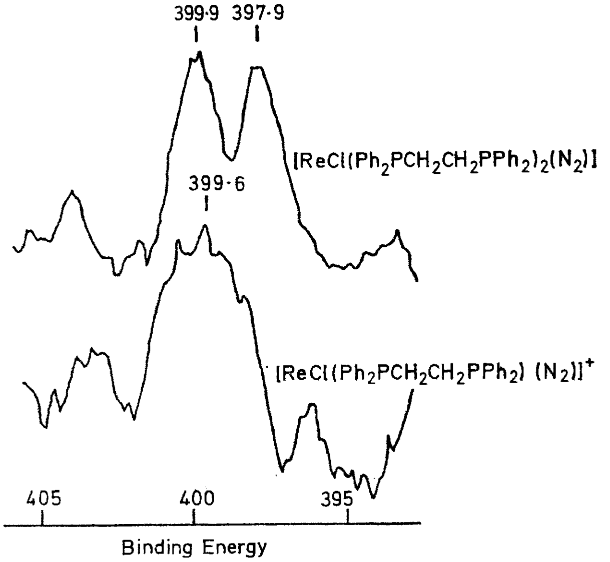
Summary Electron emission spectra from the nitrogen 1*s* orbitals of rhenium dinitrogen complexes suggest that the N–N bond has an appreciable polarity.

WE have measured the *X*-ray-induced electron emission spectra of $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ (I) and $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2][FeCl_4]$ (II). For compound (I) the 1*s* electrons of the bound dinitrogen give rise to a doublet as shown in the Figure, with maxima corresponding to electron binding energies of 397·9 ev and 399·9 ev. Compound (II) gives a broad band (half-width *ca.* 3·5ev) whose maximum is at 399·6 ev. These measurements are relative to the maximum of the unresolved carbon peak taken as 284 ev. The broad band of (II) suggests an unresolved doublet with components separated by about 1 ev. The spectra were recorded on the Varian IEE spectrometer with, typically, 300 accumulated scans collected in 200 channels over 20 ev and averaged over five adjacent channels.

From the results of Siegbahn and his co-workers[1] and of Hendrickson *et al.*[2] there appears to be a roughly linear correlation between the nitrogen 1*s* binding energies and the charge carried by the atom. The slope of the correlation line and the position of the neutral nitrogen atom depend on the method of calculation. For example, using an empirical expression based on Pauling's scale of electronegativities, it was found that a difference of one atomic unit of charge should correspond to a difference of 1*s* binding energy of *ca.* 5 ev.[1] The extended Hückel method of calculation gives a difference of 2 ev and the CNDO method gives 10 ev.[2] The extended Hückel calculations must overestimate charge polarization as they do not allow specifically for electron repulsion. The CNDO method is known to give reasonable values for dipole moments. However, the scatter of points about the CNDO correlation line is much worse than that obtained from the Pauling expression, and we, therefore, take the latter as giving the best estimate of atom charges. Thus for compound (I) we estimate the difference of charge on the two nitrogens to be 0·4 atomic units. For the rhenium cation (II) both nitrogens are more positive but the difference between the two has probably decreased to about 0·2 atomic units.

On the basis of the Pauling expression a binding energy of 399 ev corresponds to a neutral nitrogen atom. Nitrogen atoms in amines have 1*s* binding energies in the region of 398 ev. The value for benzonitrile is also 398 ev. Quaternary nitrogen atoms, on the other hand, have binding energies of 400 ev or more. The terminal nitrogen in (I) is an electron donor to strong Lewis acids such as tantalum(v) and niobium(v) chlorides. It is, therefore, unlikely to carry a large positive charge. We, therefore, assign the smaller binding energy to the terminal atom. It appears that the terminal nitrogen in (I) has a small negative charge, and that the difference in the charges on the terminal nitrogens of the two compounds is about 0·2 atomic units. The N–N stretching frequencies in the two compounds are also very different: 1980 cm^{-1} for (I) and 2060 cm^{-1} for (II). The higher frequency, therefore, occurs in the compound in which the two nitrogens have the more equal charges.



FIGURE

These results provide the first direct evidence of the charge carried by a dinitrogen molecule in a complex. In this simple model no account is taken of the charges on neighbouring atoms. For example, a positive charge on the rhenium will increase the binding energy of the 1*s* electron of the nitrogen bound to it relative to that of the terminal atom. It is difficult to estimate the magnitude of this without a detailed knowledge of the electron distribution in the molecule. Nevertheless, the fact that the separation of the two peaks of the Re^{II} compound is less than the separation for Re^{I} suggests that the charge on the rhenium does not dominate the shifts, and that the positive charges are highly delocalised.

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[1] R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Arkiv Kemi* 1967, **28**, 257.

[2] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 1969, **8**, 2642.